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THE COPPER COMPLEXES OF AMINO ACIDS, PEPTIDES AND PEPTONES[1]

II. THEIR CONFIGURATIONS AND RELATION TO THE BIURET REACTION

BY P. A. KOBER AND K. SUGIURA

I. THE FORMULAS AND CONFIGURATIONS
II. VALENCY OF PROTEIN NITROGEN
III. BIURET REACTION FOR PROTEINS
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I. THE FORMULAS AND CONFIGURATIONS

In our first paper[2] we show that monobasic α-amino acids, without exception, form complex copper salts with the general formula CuA_2, where A represents a monobasic α-amino acid. Where the amino group is in the β position, the formula is the same except that when, as in isoserine, there is a hydroxyl group in the α position, the formula is CuA. With dibasic amino acids like glutaminic, aspartic and cystinic, the formula is CuA, where A represents one molecule of a dibasic amino acid.

[1] Read in part before the Section on Organic Chemistry, International Congress of Applied Chemistry, New York, 1912.

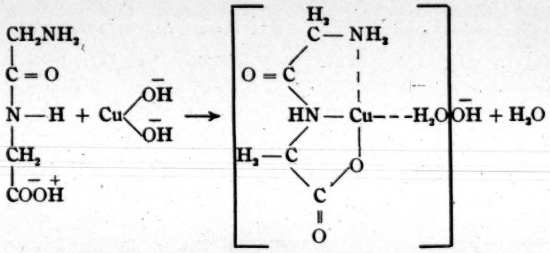
[2] J. Biol. Chem., 13, 1 (1912).

Fischer[1] found that other amino acids, where the NH_2 group was in the γ, δ or ε position, regardless of a hydroxyl group in the α position, did not form complex copper salts.

Our results on 50 polypeptides, whose copper salts were soluble, corroborate those of Fischer and Abderhalden on 5 isolated peptide copper salts, which have the general formula $(peptide)_1Cu_1$. In other words, the results show unmistakably that one molecule of peptide, whatever number of amino acids it may contain, combines with only one molecule of copper hydroxide.

The questions that remain to be solved are: How are these copper salts formed and what is their structure?

Taking glycylglycine for an example: It is interesting to attempt to picture the structure of this peptide, keeping in mind the latest work of Werner on the valency of nitrogen.



One statement we can, without much doubt, assume to be correct, namely, that one hydroxyl group is neutralized by the hydrogen of the carboxyl group, as in the case of ordinary salt formation. Although lack of material prevented our making accurate calorimetric experiments, yet comparative heats of formation of copper acetate, copper glycine and copper glycylglycine were determined.[2] Using 0.01 of a mole we found slightly less heat evolved from copper glycine than from copper acetate, and the heat from copper glycylglycine is about half of that from copper glycine. This is consistent with the equation just given. Of course we are not certain

[1] Ber. d. chem. Ges., 42, 4883 (1909).

[2] See experimental notes, p. 410.

that the heat of formation of copper glycylglycine should be equal to the heat of neutralization. It may be more or decidedly less.

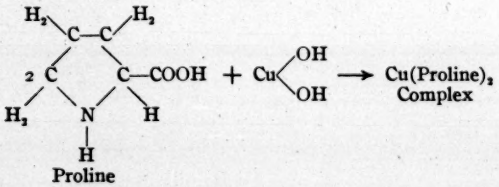
The other hydroxyl group now remains to be placed, or, in other words, it is necessary to locate the position of the other principal copper valence.

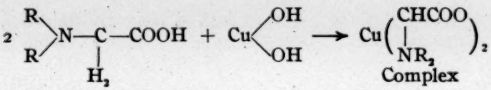
The imino group alone does not seem to be sufficient to form a copper salt. Thus bromo or chloro derivatives of dipeptides, as well as hippuric acid, and formyl derivatives of amino acids, all having an imino group but no amino group, do not form these complex copper salts with copper hydroxide.

We examined the following substances with our technic, but found no complex salts in neutral solutions:

Chloroacetylalanine	Bromoisocaproylglycine
Chloroacetylaminobutyric acid	*n*-Bromocaproylglycine
Chloroacetylvaline	Bromocaproylleucine
Chloroacetyl-*l*-leucine	*d*-Bromoisocaproyl-*d*-leucine
Chloroacetyl-*l*-tyrosine	Formylalanine
Bromopropionylglycine	Formyl-*d*-leucine
Bromopropionyl-*d*-alanine	Formyl-*l*-tyrosine
l-Bromopropionyl-*d*-alanine	Hippuric acid
l-Bromopropionyl-*l*-alanine	Benzoyl-*d*-leucine
Bromobutyrylglycine	
Bromovalerylglycine	

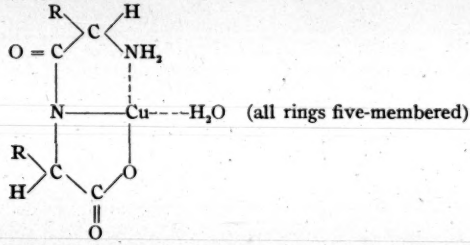
These facts show a decided difference between an $R—NH_2$ and $R—C(=O)—NH—$ group, particularly when there are no other nitrogen atoms in the compound. When, however, positive radicals such as $CH_3—$, $C_2H_5—$, etc., take the place of one or more of the hydrogen atoms of the amino group, the property of forming complexes is unimpaired, e. g.,





R being H, CH_3, C_2H_5, C_3H_7, etc.., as in sarcosine, diethylglycine, diethylalanine, etc.

As we mentioned before, an amino group in the γ, δ or ε position will not form a complex salt,[1] because it seems that if a salt contains a ring of seven or more members it is unstable. Werner,[2] Pfeiffer,[3] L. Tschugaeff,[4] Blau,[5] Dittley[6] and Piloty and Schlenk,[7] have found that only five- or six-membered rings in metallic complexes are stable. Therefore we may assume that for di- and tripeptides the free amino group is essential, directly or indirectly, to the formation of copper salts (see page 396); and without deciding on all questions of valence, the structure of a dipeptide copper salt is probably as follows:



(all rings five-membered)

(NOTE.—Dotted lines here represent the secondary valences of copper.)

Bromo, chloro, and other derivatives of tripeptides, which have two imino groups but no amino groups, also give very little of the copper salt with our technic in neutral solution. The tables below show this in the second and third columns.

[1] Fischer and Zemplén: Ber. d. chem. Ges., **42**, 4883 (1909).
[2] Werner: Neuere Untersuchungen, **8**, 280 (1911).
[3] Pfeiffer and Hannan: Ber. d. chem. Ges., **36**, 1065 (1903).
[4] L. Tschugaeff: *Ibid.*, **39**, 3197 (1906).
[5] Blau: Monatsh. Chem., **19**, 690 (1898).
[6] Dittley: Ann. Chem. (Liebig), **341**, 300 (1906).
[7] Schlenk: Uber Metal-Isobutyradine und ihre Salze; Inaug.Dissert., München, 1905.

Bromotripeptides

Substance	Weight of sample Grams	CuO in filtrate without alkali Grams	Complex color	CuO in filtrate after adding 20 cc. N NaOH Grams	Color	Theoretical weight of CuO, calculated for this sample Grams	Per cent. of theoretical of CuO in alkaline filtrate for formula $(peptide)_1 Cu_1$
Bromoisocaproylglycyl-glycine	0.1008		none	0.0083	complex	0.0259	32.0
Bromo-*n*-caproylglycyl-glycine	0.1001		none	0.0175	complex	0.0258	67.8
Bromobutyrylglycylglycine	0.0982		none	0.0218	complex	0.0278	78.4
Bromoisocaproylleucyl-leucine	0.1012		none	0.0060	complex	0.0191	31.4
Bromovalerylglycylglycine	0.0613		none	0.0052	complex	0.0165	31.5
d-Bromocaproylglycyl-*d*-alanine	0.0558		none	0.0092	complex	0.0137	67.2
d-Bromocaproyl-*d*-alanyl-*d*-alanine	0.0514		none	0.0073	complex	0.0121	63.3
Bromopropionylglycyl-glycine	0.1009		none	0.0230	complex	0.0301	76.4

Chlorotripeptides

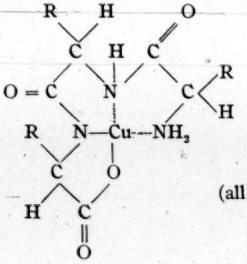
Substance	Weight of sample Grams	CuO in filtrate without alkali Grams	Complex color	CuO in filtrate after adding 20 cc. N NaOH Grams	Color	Theoretical weight of CuO, calculated for this sample Grams	Per cent. of theoretical of CuO in alkaline filtrate for formula $(peptide)_1 Cu_1$
Chloroacetylglycylleucine	0.0712		none	0.0164	complex	0.0214	76.6
Chloroacetyl - *l* - alanyl - glycine	0.0708		none	0.0207	complex	0.0252	82.1
Chloroacetylglycylvaline	0.0924		none	0.0230	complex	0.0294	78.2
Chloroacetylglycylglycine	0.1018	0.0164 bluish green filtrate	none	0.0317	complex	0.0388	81.7
Chloroacetylleucylglycine	0.1008		none	0.0190	complex	0.0302	62.9
Chloroacetylglycylalanine	0.1012	0.0139 bluish green filtrate	none	0.0293	complex	0.0362	80.9
Chloroacetylglycylasparagine	0.1003		none	0.0199	semibiuret color	0.0300	66.3
Chloroacetylvalerylglycine	0.1004		none	0.0157	complex	0.0319	49.2

Bromotetrapeptides

Substance	Weight of sample Grams	CuO in filtrate without alkali Grams	Complex color	CuO in filtrate after adding alkali Grams	Color	Theoretical weight of CuO, calculated for this sample Grams	Per cent. of theoretical of CuO in alkaline filtrate for formula $(peptide)_1 Cu_1$
Bromo - *n* - caproyldi - glycylglycine	0.1018		none	0.0185	semibiuret	0.0222	83.3
Bromoisocaproyldiglycylglycine	0.0532		none	0.0109	semibiuret	0.0116	94.0
Bromovaleryldiglycylglycine	0.1008	0.0048 bluish green filtrate	none	0.0224	semibiuret	0.0228	98.2
Bromopropionyldiglycylglycine	0.0572		none	0.0133	semibiuret	0.0140	95.0
Bromobutyryldiglycylglycine	0.0506		none	0.0113	semibiuret	0.0119	95.0
"Bromocaproylpeptone"	0.1007		none	0.0113	biuret		

In alkaline solution, however, quite appreciable amounts of complex copper salts were formed and a possible reason for this will be discussed on page 396.

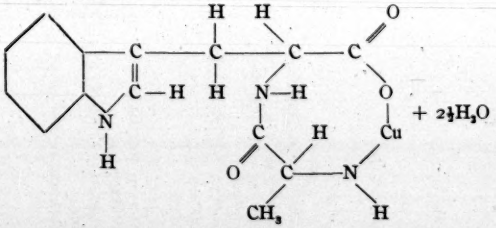
Here, too, the solubility of copper hydroxide in neutral solution is dependent to a large extent upon the presence of a free amino group, which serves to produce a stable ring formation,



(all rings five-membered)

These facts would seem to indicate that the free NH_2 group is necessary for the neutralization of the second OH group. For di-, tri- and tetrapeptides this is true; the NH_2 group or its alkyl derivative is essential to the formation of "neutral" complexes, but, as we hope to show later, only indirectly.

The only attempt to picture one of these copper salts was made by Abderhalden,[1] who gave alanyl-*l*-tryptophan the following structure:



Thus one of the hydrogen atoms of the amino group is sup-

[1] *Loc. cit.*

posed to be neutralized by the second OH ion of the copper, and an eight-membered ring is formed. Aside from the improbability of the formation of such a ring, it seems to us doubtful that, as this conception holds, the NH_2 group should be no longer basic, should form no salts such as hydrochlorides, but should on the contrary have a replaceable hydrogen atom. These peptides do form hydrochlorides, give off very little heat in forming copper salts, and in a study of the valences involved there is found no reason to believe that the hydrogen of the NH_2 group is replaceable. Nitrous acid acts (Van Slyke's method) fully as well on the free amino nitrogen of these peptides as on that of the amino acids, and according to Abderhalden's conception there is no reason why the free amino acids should not act as dibasic acids also. But this is contrary to many facts.

These considerations, together with facts cited in reference to ring formation, lead us to believe that in peptides, as in the free amino acids themselves, only the secondary valences of copper are connected with the amino (NH_2) group.

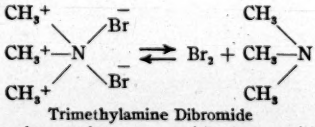
We are therefore forced to the conclusion *that in peptides the imino group is instrumental in combining with the second OH ion of the copper*. There is some evidence to support this. The tables given above show that bromo and chloro acid *derivatives of amino acids*, with only one imino nitrogen and no amino nitrogen, give practically *no complex*[1] *copper* salts *in neutral or alkaline solution*, while *similar derivatives of dipeptides* with two imino nitrogens dissolve no copper to form complexes in neutral solution, but in *excess of hydroxyl ions* tend to dissolve *one molecule of copper hydroxide. Similar derivatives of tripeptides* with three imino nitrogens also give no appreciable amount of complex in neutral solution, but *with alkali also give a complex (involving one molecule of copper hydroxide) which is macroscopically of the same color as alkaline tripeptide salt, suggesting a biuret color*. In these substances we can substitute the free NH_2 group and yet produce the same effects. How is this to be explained?

[1] A trace of copper is dissolved, but we feel justified in not calling it a complex salt.

II. VALENCY OF PROTEIN NITROGEN
(The Basis for Configurations)

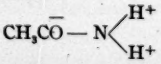
The chemistry of protein has to some extent resolved itself into the chemistry of nitrogen. It is clear from a review of these salts that certain conditions of nitrogen are associated with certain marked and characteristic colors. For example, a dipeptide copper salt, containing two nitrogen atoms, gives in an alkaline solution a color similar to that of an ammonia complex; a tripeptide, containing three nitrogen atoms, gives a deep bluish violet color; while a tetrapeptide, with four nitrogen atoms, gives a red phenolphthalein color, indicating the additive influence of a nitrogen group on the complex.

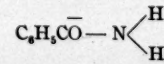
A brief review of the valency[1] of nitrogen in the ammonia group is not out of place here, as it is the only basis for these configurations that we can propose. In ammonia we have three positive hydrogen atoms, or three positive valences. In ammonium compounds, such as ammonium chloride, the nitrogen has at least four valences and perhaps five. In other words, nitrogen is capable of combining, directly or indirectly, with five monovalent elements, and not more. If one is negative—and there must always be one negative element to a pentavalent nitrogen—and the other four positive, the group is quite stable. A nitrogen compound containing two negative and three positive elements is unstable, but capable of existence in equilibrium with an excess of one of the negative elements.[2]



Trimethylamine Dibromide

The amides also, such as acetamide, benzamide, etc., belong to this class:

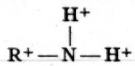




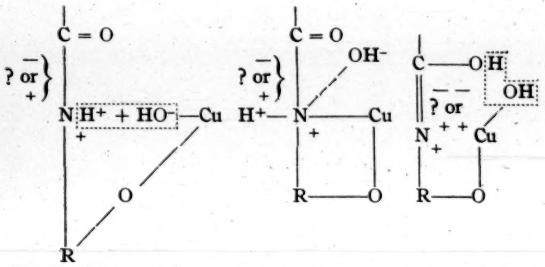
[1] Taken mostly from H. Kauffmann's "Die Valenzlehre," and from Werner's "New Ideas in Inorganic Chemistry."

[2] Remsen: THIS JOURNAL, **18**, 91. Hantzsch and Graef: Ber. d. chem. Ges., **38**, 2154 (1905).

and form unstable hydrochlorides. Here also there would be two negative and three positive valences. Therefore in the amino acids we must consider the nitrogen as having practically three positive valences:



Keeping all these facts in mind, we can conceive of the imino group combining with the copper in three ways:

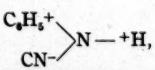


I. Trivalent Nitrogen

II. Pentavalent Nitrogen

III. Trivalent Nitrogen

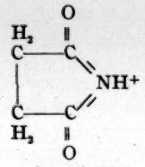
So far we have found no reason for believing that the hydrogen of the imino group of a peptide can be replaced by copper. If the nitrogen has one negative group or valence (Reaction I), as in phenylcyanoamide,[1]



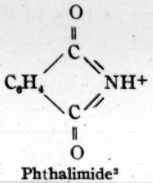
the hydrogen becomes replaceable.

If nitrogen has two negative groups, as in

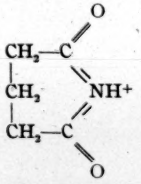
[1] From H. Kauffman: Die Valenzlehre, p. 351.



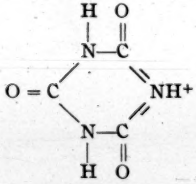
Succinimide[1]



Phthalimide[2]



Glutarimide[3]



Cyanuric Acid[4]

the hydrogen atom also becomes replaceable.

On the other hand, biuret[5] and the other amides whose nitrogens have two positive and one negative valences seem not to have a replaceable hydrogen atom.

Hantzsch[6] and E. Voegelen have shown that the amides $R.CONH_2$ are quite neutral nonelectrolytes, which do not, to any appreciable extent, form salts in aqueous solution with alkalies or acids.

Therefore if we can expect the imino groups $\left(R-C\begin{matrix}=O\\ \diagdown NH-\end{matrix}\right)$ to have a replaceable hydrogen atom, we should certainly expect it in an amide group $\left(R-C\begin{matrix}=O\\ \diagdown NH_2\end{matrix}\right)$ where two hydrogen atoms are available. As Van Slyke[7] has shown with asparagine, and as we have determined with the following amides and imino derivatives, the amide nitrogen does not liberate free nitrogen with nitrous acid, and thus in this respect also resembles the imino group.

[1] Landsberg: Ann. Chem. (Liebig), **215**, 200.
[2] *Ibid.*
[3] Bodtker: Dissertation.
[4] Beilstein: Handb. org. Chem., I, 1267.
[5] Schiff: Ber. d. chem. Ges., **29**, 299 (1896).
[6] *Ibid.*, **34**, 3143 (1901).
[7] J. Biol. Chem., **9**, 185 (1911).

Amides and Imino Substances

Amino-nitrogen determinations, using Van Slyke's method[1]

Substance	Weight of sample	Cc. nitrogen evolved, standard conditions		Cc. nitrogen on blank tests (ave.), standard conditions		Cc. nitrogen corrected for controls		Per cent. amino nitrogen	Per cent. total nitrogen
Amides	Grams	10 min.	20 min.	10 min.	20 min.	10 min.	20 min.		
Acetamide	0.1161	1.47	1.84	0.65	0.73	0.82	1.11	0.61	23
Chloroacetylasparagine	0.2011	0.64	0.77	0.65	0.73	....	0.04	0.01	13
Bromopropionylasparagine	0.1029	0.87	0.91	0.65	0.73	0.22	0.18	0.10	10
Bromocaproylasparagine	0.1047	0.72	0.76	0.65	0.73	0.07	0.03	0.01	9
Benzoylasparagine	0.1061	0.91	1.00	0.65	0.73	0.26	0.27	0.15	16
Biuret	0.1070	1.25	1.61	0.65	0.73	0.60	0.88	0.51	40
Imino derivatives									
Formyl-*d*-leucine	0.1001	0.62	0.71	0.65	0.73	....	....	....	8
Benzoylleucine	0.1031	0.62	0.67	0.65	0.73	....	....	....	5
Hippuric acid	0.1013	0.64	0.73	0.65	0.73	....	....	....	7
Cyanuric acid	0.1048	0.73	0.86	0.65	0.73	0.08	0.13	0.07	32

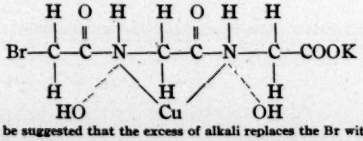
[1] These determinations were made by Mr. E. N. Rosenfeld, in this laboratory.

But if we consider that the imino group in peptides has only positive valences, the presence of replaceable hydrogen would be exceptional and unexpected. If we consider the imino derivatives as having one negative group (and this would favor or permit of one hydrogen atom being replaceable), then a bromo or chloro derivative of a di-, tri-, or tetrapeptide ought to give a considerable quantity of dibasic salt. This it does not do. One amino substance, containing only one nitrogen atom, and acting toward copper as a dibasic substance, should be considered in this discussion:

Isoserine or β-amino-α-hydroxypropionic acid, $\overset{-}{\underset{+}{CH_2NH_2}}\,\overset{-}{\underset{+}{CHOH}}\,\overset{-}{\underset{+}{COOH}}$

The question here too is, is it the hydrogen of the NH_2 group or of the hydroxy group that is replaceable? We believe with Fischer that the hydrogen of the hydroxy group acts as an acid ion, and that the NH_2 group does not participate in the neutralization of the second OH group of the copper. If it did participate, the nitrogen group would be negative, and therefore would not show the usual blue color characteristic of a complex. The color, however, does not seem to differ from that of most amino acid copper complexes.

We are therefore forced to the conclusion that the *second principal valence of copper combines only with the partially basic nitrogen of the imino group* (Reaction II), and in substances like chloro and bromo acid derivatives of amino acids the nitrogen is no longer basic, and therefore is incapable of forming complexes. The same is true of similar derivatives of dipeptides in neutral solution, but in excess of alkali[1] these substances are at least partially basic.



[1] It might be suggested that the excess of alkali replaces the Br with a OH group, but qualitative tests have not shown any appreciable hydration.

This means that a complex is formed in these derivatives only when in the presence of an excess of negative ions, because of the fact that the bromine atom gives a higher negative charge to the third valence of the nitrogen, and in this respect the compound is similar to trimethylamine dibromide.

The exact position of the second OH ion from the copper remains to be determined. According to Werner, if the reaction II occurs, the OH group is ionizable, and should therefore give an alkaline solution. This we have not found, yet our failure to find any alkalinity may be due to the fact that there are two or more nitrogen atoms that are capable of combining with this OH group, thereby reducing its concentration in solution to an inappreciable amount. We hope to say more on this subject later.

III. BIURET REACTION FOR PROTEINS

As we mentioned in the first paper, the biuret reaction is considered the most reliable of the protein tests. Speaking chemically, what does this reaction mean, what configuration does it involve? By *biuret color* is generally meant a violet or red color, obtained with a small amount of copper salt and a good excess of alkali. Often a color is called *biuret* when it is mixed with a considerable amount of ordinary copper-complex blue, and considerable confusion has arisen from this misuse of terms. On the basis of the preceding data we wish to propose the following theory in reference to the biuret reaction, and to show the direction along which our experiments have led us.

For the present we shall use the following terms: (*a*) *Biuret color;* a purple-red, resembling somewhat an alkaline phenolphthalein solution in color. Colors having a bluer tint we shall term (*b*) *partial biuret*, or *semibiuret*, as some are probably mixtures of pure *biuret* and ordinary complex-blue. Another term we should like to fix: (*c*) *Biuret reaction* of a peptide; the color reaction obtained on adding a large excess of alkali to the peptide when it is *completely combined* with copper, i. e., the color reaction of its *alkaline copper salt.*

If we classify the peptides according to these terms we find that:

I. All *simple dipeptides* made from monoamino acids, excluding their amide derivatives, give about the same color with copper in alkaline solution—a deep blue color like that of the ammonia-copper complex.

II. The neutral copper salts of all *tripeptides*, made from monoamino acids, excluding their amide derivatives, and of all *amides of dipeptides* change color on the addition of excess of alkali. They give shades of the "semibiuret" color, the shade varying with the constituent amino acids and the temperature.[1]

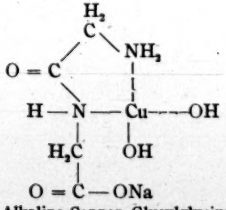
III. The color of the neutral copper salts of all *tetrapeptides* of monoamino acids, and of *amides of tripeptides*, changes on addition of excess of alkali from the deep blue of their neutral copper complex to the purple-red "biuret color."

To summarize:

I. When a substance is so combined with copper that *only two nitrogen atoms* are connected with the copper in a ring formation,[2] stable in excess of alkali, the result is a *deep blue color*, resembling that of the copper-ammonia complex.

For example:

(*a*) All simple dipeptides made from monoamino acids, like

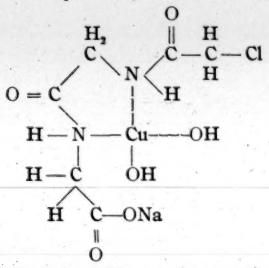


Alkaline Copper Glycylglycine

(*b*) All carboxyl derivatives of simple dipeptides made from monoamino acids; such as

[1] The amount of biuret color seems to increase with rise in temperature, which fact would suggest that an equilibrium exists between the blue and red substances.

[2] By "ring formation" we mean formations of not more than six members.

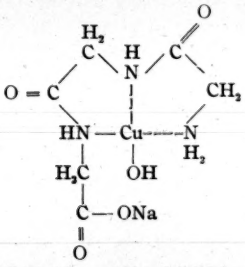


Alkaline Copper Chloroacetylglycylglycine

II. When *three nitrogen atoms* are connected with copper in a ring formation that is stable in excess of alkali, a "*semi-biuret*" *color* is produced.

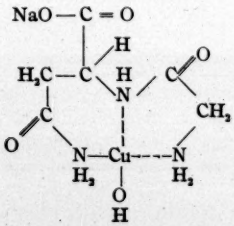
For example:

(*a*) All simple tripeptides made from monoamino acids, such as



Alkaline Copper Glycylglycylglycine

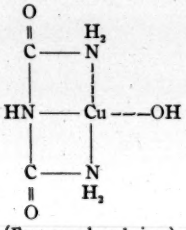
(*b*) All amides of simple dipeptides made from monoamino acids, such as



Alkaline Copper Glycylasparagine

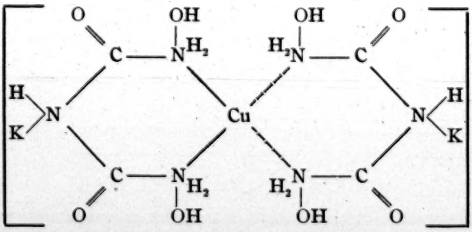
(*c*) Various diamides, and other substances studied by Schiff. Some of these, when fully combined with copper, will probably give a blue complex color, and they probably have only two nitrogen atoms connected in the ring with the copper atom and belong to the first class of salts. (Owing to our lack of quantitative data on the subject, however, we suggest only one configuration, that of biuret.) Furthermore, when the amount of substance is in large excess, as is usually the case when the biuret test is made, two or more molecules of the substance may combine to form a mixture of nitrogen complexes. Thus:

A "semibiuret" complex (see experimental notes, page 410)



(Four-membered rings)

and a "true biuret" complex:[1]



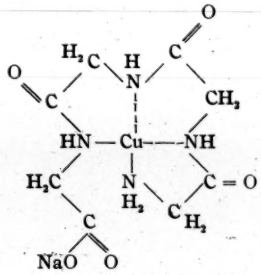
III. When *four nitrogen atoms*, as in the case of biuret copper just shown, are connected with the copper in a ring formation that is stable in excess of alkali, a *purple-red color*

[1] Schiff's compound with our idea of structure, which fits his analyses. Ber. d. chem. Ges., **29**, 298 (1896). (See discussion, page 394).

resembling that of phenolphthalein in alkaline solution is produced. *This is the true biuret color.*

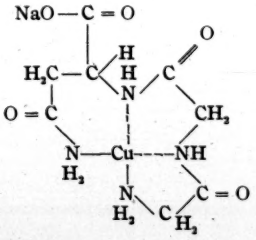
Examples:

(*a*) All simple tetrapeptides made from monoamino acids, as



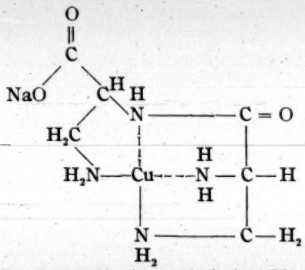
Alkaline Copper Triglycylglycine

(*b*) All amides of simple tripeptides made from monoamino acids, as



Alkaline Copper Diglycylasparagine

(*c*) Some diamino acid dipeptides, as



Alkaline Copper Diaminopropionic Acid Dipeptide

Fischer[1] found that this substance was the only dipeptide giving a strong biuret reaction, and was inclined to doubt the identity and purity of the substance. If our supposition is correct, there can be no question as to the identity of this substance, as our results support Fischer's work. But our work has not yet made clear which of the two possible isomers it is that produces the biuret configuration.

IV. A REVIEW OF PREVIOUS WORK ON ALLIED COMPOUNDS

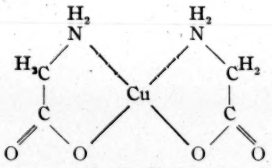
So far we have given the results of our own investigations and those of Fischer and Abderhalden, and have given a chemical structure of the "biuret configuration." There was *much pioneer work* done by Schiff, Tschugaeff, Ley and Werner, and we append here a discussion, necessarily brief, of their work in reference to ours.

Schiff,[2] who studied very many substances containing $CONH_2$ and NH groups, for the most part qualitatively, in order to find a structural basis for the biuret reaction, came to the following conclusion: "Als Biuretreaction sollte man systematisch nur diejenige bezeichnen welche durch Kupfer- oder Nickelsalze mit Aminoamiden oder Diamiden erhalten wird, welche schliesslich auf die drei Grundformen: Biuret, Oxamid und Malonamid und ihre Substitutionproducte zurückgeführt werden können."

[1] Fischer: Untersuchungen über Aminosäuren, Polypeptide und Proteine, p. 50.
[2] Schiff: Ann. Chem. (Liebig), **299**, 240; **303**, 73–87.

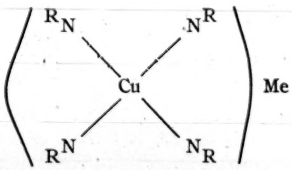
Some of the colors Schiff called biuret belong in all three of our classes; and until the amount of copper is determined in connection with the character of the color, very little can be said of possible configurations. We have every reason to believe that when this is done the results will, as we have indicated with biuret itself, be in accord with the biuret configuration given above.

Ley[1] believes that the copper complexes of amino acids are ring formations, as in

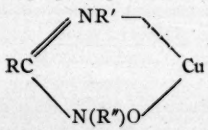


Copper Glycine

and that the abnormal color is due to the action of secondary valences. When both secondary and principal valences are connected with the copper, a red or violet-red color results, and the substance has, according to Ley, the following configuration:

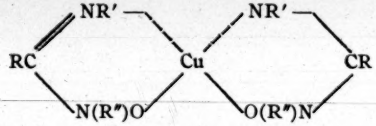


These ideas are fully supported by our work on the peptides, but we are not ready to accept his structure of the copper salt of 1-phenyl-3-benzylhydroxyformamidine, which he gives as

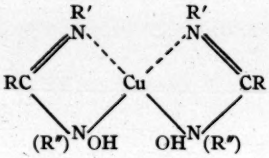


[1] Ley: Z. Electrochem., **1904**, 954; **1905**, 585. Ber. d. chem. Ges., **40**, 705; **42**, 366.

The analysis of this red copper salt is consistent with the formula $(C_{14}H_{13}ON_2)_2Cu$, and according to Ley the formula should be written



The fact that the salt is red leads us to doubt that its structure should be such. If our ideas, as stated in connection with the peptides, are correct, this salt has the following structure:



This conception is more consistent with the very weak acid properties of the hydroxyformamidine.

Tschugaeff[1] found that succinimide combined with copper hydroxide and amines to form crystalline salts. Those with three nitrogen atoms attached to the copper (two succinimides and one amine) gave crystals of a deep blue-violet to violet color. They are as follows:

$$\left(\begin{matrix}CH_2-CO\\ |\\ CH_2-CO\end{matrix}\!\!>\!N\right)_2CuNH_3 + 3H_2O$$

$$\left(\begin{matrix}CH_2-CO\\ |\\ CH_2-CO\end{matrix}\!\!>\!N\right)_2CuCH_3NH_2 + 3H_2O$$

These salts on dissolving in water yield a deep blue color, no doubt the results of hydrolysis; the imide nitrogen, being negative, dissociates in aqueous solution, as in the case of ordinary copper salts. *The bluish violet color* of the *crystals*,

[1] Tschugaeff: Ber. d. chem. Ges., **37**, 1480; **38**, 2904; **40**, 1977.

and *the three nitrogen atoms* attached to the copper, would cause these salts to be *included in our second class*, the class *giving a "semibiuret" color*. Those with four nitrogen atoms connected with the copper atom, two being of the imide and two of the amines, yield brown-red or "copper-red" crystals. They are as follows (Su = succinimide):

$(Su)_2Cu.2(NH_3)$	$(Su)_2Cu.2(C_9H_4NH_2)$ (tert.)
$(Su)_2Cu.2(CH_3NH_2)$	$(Su)_2Cu.2(C_5H_{11}NH_2)$ (iso)
$(Su)_2Cu.2(C_2H_5NH_2)$	$(Su)_2Cu.2(C_6H_{13}NH_2)$ (normal)
$(Su)_2Cu.2(C_3H_7NH_2)$	$(Su)_2Cu.2(C_3H_5NH_2)$
$(Su)_2Cu.2(C_4H_9NH_2)$ (normal)	$(Su)_2Cu.2(C_9H_{15}CH_2NH_2)$[1]
$(Su)_2Cu.2(C_4H_9NH_2)$ (iso)	$(Su)_2Cu.2(CH_3)_2NH$
$(Su)_2Cu.2(C_4H_9NH_2)$ (sec.)	$(Su)_2Cu.2(C_5H_5N)$[2]

Tschugaeff found the following salts, which also have a red color (Ph = phthalimide, Gl = glutarimide):

$(Ph)_2Cu.2(NH_3)$
$(Gl)_2Cu.2(C_6H_5CH_2NH_2)$

These red salts, on dissolving in water, give also a deep blue color, due no doubt to hydrolysis. Tschugaeff finds that the following tetraimide copper salts also yield the biuret color:

$K_2Cu(Su)_4.6H_2O$, light red-violet
$Rb_2Cu(Su)_4.2H_2O$, red-violet
$CsCu(Su)_4.2H_2O$, red-violet

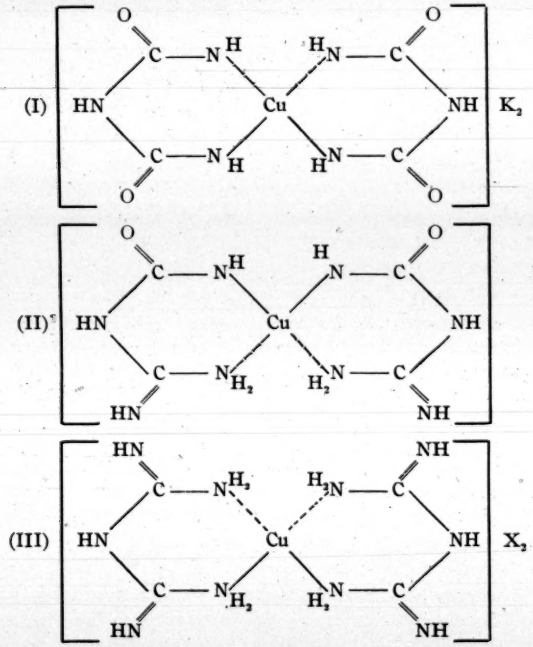
but his sodium and lithium compounds unexpectedly gave only a blue color:

$Na_2Cu(Su)_4.5H_2O$, blue
$Li_2Cu(Su)_4.H_2O$, blue

The reddish color of most of these salts, and the presence of *four nitrogen atoms connected to the copper*, cause these salts to be *included in our third class of substances giving a "true biuret" color*. From our experience this decided difference between the sodium and potassium salts seems most improbable; and we think it likely that the former is a molecular substance, while those having the red color are atomic complexes.

[1] Camphylamine compound.
[2] Pyridine compound.

That Tschugaeff came to practically the same conclusion in regard to the "biuret configuration" can be seen from his structure of red copper salts of biuret (I), dicyanodiamidine (II), and diguanidine (III):



These configurations are, we believe, very nearly correct, but we cannot come to the same conclusion as regards some of the details. As may be seen in (I), each of the four amides has lost one hydrogen atom, which Tschugaeff believes are removed by neutralization. Schiff's[1] analyses do not support

[1] Schiff: Ber. d. chem. Ges., **39**, 298.

this idea, and we have shown on page 393 our reasons for not accepting it. The same may be said of Formula (II). Owing to lack of analytical data we defer discussing other minor points.

V. GENERAL DISCUSSION AND CONCLUSIONS

On reviewing all the complexes, we find that about *25 substances* containing *one copper* and *four nitrogen atoms* in the molecule *give a "red biuret" color*; that about *30 substances* containing *one copper* and *three nitrogen atoms* give a *"semibiuret" color*; and that about *25 substances*, containing *one copper* and *two nitrogen atoms* give a *deep blue color*. Slight variations in color in occasional substances may be due to the influence of the various groups or radicals, as well as to variations in temperature. We intend to study this phase of the question spectrographically in the near future.

That the amide, imide, imino and amino substances combine coördinately (in the sense used by Werner), there is little doubt, but several points remain to be cleared up, i. e., the exact fate of the second OH group of the copper. According to Werner, it ought to be ionizable, and therefore render the solution alkaline. That most of these peptides are stable in excess of alkali is in favor of that hypothesis.

Summary

We have found that:

I. All *simple dipeptides* made from monoamino acids (excluding their amide derivatives), and *their carboxyl derivatives*, give about the same color with copper in alkaline solution—a *deep blue color* like that of the ammonia-copper complex.

II. The neutral copper salts of all *tripeptides*, made from monoamino acids, and *their carboxyl derivatives* (excluding their amide derivatives), and of all *amides of dipeptides* change color on the addition of excess of alkali. They give shades of the *"semibiuret" color*, the shades varying with the constituent amino acids and the temperature.

III. The color of the neutral copper salts of all *tetrapep-*

tides of monoamino acids, and of *amides* of *tripeptides*, change on addition of excess of alkali from the deep blue of their neutral copper complex to the *purple-red "biuret color."*

IV. Our experiments seem to show that a *true biuret* reaction can occur only when *four nitrogen atoms* are so arranged that they can *combine "coördinately" with the copper* in an *alkaline solution.*

V. A *semibiuret reaction* can occur only when *three nitrogen atoms* are so arranged that they can combine *"coördinately"* with the *copper* in *an alkaline solution.*

VI. EXPERIMENTAL

Molecular Weight Determinations by the Freezing Point Method

The determination of the molecular weights of copper salts involves several considerations:

(1) Purity of the copper salt. The only method of purification that would insure the purity of these substances is recrystallization. With the exception of a few peptides, this method is very difficult to follow, as most copper salts do not crystallize readily. A few salts, however, such as leucylglycine and leucylleucine, crystallize easily.

(2) Concentration of solute. The copper salts of dipeptides referred to above dissolve only to a slight extent, and their insolubility does not permit of many variations in the concentration of the solute.

The results show that in leucylglycine copper the amount of free OH ion is quite small, whereas in glycylglycine copper it may be quite appreciable. They also show clearly enough that two molecules of copper complexes are not combined into one molecule in aqueous solutions.

Substance	*W*	*K*	*L*	Δ	*M* (found)	*M* (calculated)
Glycine	0.1969	1850	24.39	0.199	75.0	75.07
Glycine	0.2005	1850	23.88	0.208	74.7	75.07
Copper glycylglycine(OH)	0.1969	1850	25.12	0.099	146.0	211.7
Copper glycylglycine(OH)	0.1952	1850	24.54	0.090	164.0	211.7
Copper glycylphenylglycine(OH)	0.1001	1850	24.07	0.028	281.0	323.6
Copper leucylglycine(OH) H_2O	0.1960	1850	28.87	0.031	405.0	285.8
Copper leucylglycine(OH) H_2O	0.0682	1850	24.54	0.021	353.0	285.8
Copper leucylglycine(OH) H_2O	0.1451	1850	24.42	0.035	316.0	285.8
Copper leucylglycine(OH) H_2O	0.2017	1850	24.75	0.052	290.0	285.8
Copper leucylglycine(OH) H_2O	0.2003	1850	24.79	0.062	241.0	285.8
Copper leucylglycine(OH) H_2O	0.2043	1850	23.72	0.055	290.0	285.8
Copper leucylglycine(OH) H_2O	0.2931	1850	23.65	0.077	298.0	285.8

$$M = \frac{KW}{\Delta L}$$

M = molecular weight.
W = weight of substance dissolved.
K = constant of solvent, water.
L = weight of solvent, water.
Δ = depression of freezing point.

Biuret

We made biuret copper in two ways:

First, about 0.1000 gram of biuret was dissolved in 20 cc. normal sodium hydroxide. While constantly stirring in ice mixture, cold copper hydroxide was added little by little until the red color of biuret changed slightly toward a blue. The biuret copper was then dissolved with acetic acid and titrated as usual.

The theoretical amount of copper oxide, according to Schiff's work, should be one molecule for every two of biuret. As the following tables show (Specimens A), practically this result was obtained.

Second, about 0.1000 gram of biuret was dissolved in different amounts of normal sodium hydroxide—30, 40 and 50 cc.—cooled in ice and mixed with *an excess of cold copper hydroxide*. After stirring for 5 or 10 minutes and filtering through a Gooch crucible,[1] the amount of copper was determined by titration with the usual technic. The results in the following table (Specimens B) are consistent with the formula $(Biuret)_1Cu_1$:

	Substance	Weight of sample Gram	CO_2 free N NaOH used Cc.	CuO in[4] filtrate Gram	Theoretical wt. of CuO calc. for this sample Gram	Per cent. CuO in alkaline filtrate to theory
A	Biuret	0.1011	20	0.0355	0.0387[2]	91.5
A	Biuret	0.1024	20	0.0371	0.0391[2]	94.9
B	Biuret	0.1004	30	0.0696	0.0768[3]	90.1
B	Biuret	0.1008	40	0.0744	0.0772[3]	96.4
B	Biuret	0.1010	50	0.0747	0.0773[3]	96.6

Calorimetric Measurements on the Heat of Formation of Copper Salts

Since each of these copper salts contains one atom of copper, it is natural to expect that if their formation is dependent on the neutralization of copper hydroxide, the heat of formation will in each case be the same. We have not attempted accur-

[1] Filter paper cannot be used with biuret copper. Therefore a Gooch crucible with an asbestos mat was employed.

[2] For two molecules of biuret to one of copper.

[3] For one molecule of biuret to one of copper.

[4] Blank tests on the reagents were made and corrections applied.

ate experiments on this question, as they would require the use of too much expensive material. The following table, therefore, gives only a qualitative demonstration of the relative amounts of heat given off in the formation of copper acetate, copper glycine and copper glycylglycine when only 0.01 mole is formed.

The experiments were carried out in a Dewar flask, which served very well as a calorimeter.

Substance	Molecular weight	Weight of 0.01 mole Grams	Gross calories per 0.01 mole of salt
Copper hydroxide	97.6	0.976	..
Acetic acid	60.0	0.600	44
Glycine	75.07	0.7507	26
Glycylglycine	132.14	1.3214	13

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A STUDY OF THE CONDUCTIVITY AND DISSOCIATION OF CERTAIN ORGANIC ACIDS IN AQUEOUS SOLUTION AT DIFFERENT TEMPERATURES

BY A. SPRINGER, JR., AND HARRY C. JONES

INTRODUCTION

A careful review of the work previously done on the conductivity and dissociation of organic acids in aqueous solution has already been made by White and Jones[1] and by Wightman and Jones;[2] so that any historical sketch that we might give would be superfluous. We shall therefore proceed at once to the experimental part of our work, and, in the discussion which follows, reference will be made to all important articles having direct bearing on our results.

This particular investigation has been in progress for somewhat more than two years. During the first year, conductivity measurements were made at temperatures between zero and thirty-five degrees. During the second year the conductivities of the same acids—as well as some already

[1] THIS JOURNAL, **44**, 159 (1910).
[2] *Ibid.*, **46**, 56 (1911).

used by White and Jones at lower temperatures—were taken at temperatures ranging from thirty-five to sixty-five degrees. The two sets of results at thirty-five degrees were compared, and by this method we had a means of comparing the work of the two different years. Some of these agreements and disagreements will be tabulated in another place. The two sets of measurements, for any given acid, were made with different apparatus, different solutions, usually with different specimens of the acid, and frequently by different investigators.

Reagents

The water used in all this work was prepared in the manner always employed in this laboratory and adequately described by Jones and Mackay.[1]

The acids used were obtained in most cases from Kahlbaum. They were, with one exception, purified by filtration and recrystallization from conductivity water. Before weighing, they were always carefully dried over sulphuric acid in a vacuum desiccator. Their melting points were taken, whenever possible, as a test of their purity. The most concentrated solution used was made up by direct weighing and standardized by titration against a solution of sodium hydroxide of known concentration. The only acid that we could not treat in this manner was dichloroacetic. This we did not purify at all, it being the best obtainable (distilled from chloral). Being a liquid at ordinary temperatures and hygroscopic, it could not be weighed accurately. The mother solution was, therefore, prepared by the usual titration method.

Apparatus

The conductivity cells were of the type used by Jones and Bingham.[2] Briefly, these have platinum electrodes (coated with platinum black) attached to glass tubes containing mercury, the tubes being sealed into ground-glass stoppers. A special cylindrical type of cell[3] was used for determining the conductivity of the water.

[1] THIS JOURNAL, **19**, 91; Z. physik. Chem., **22**, 237 (1897).
[2] THIS JOURNAL, **34**, 493 (1905).
[3] *Ibid.*, **45**, 282 (1911).

The cell constants were taken in the manner described by White and Jones. During the low temperature work the cells were standardized about once a month. While working at elevated temperatures this was done even more frequently.

When this investigation was begun, an ordinary Wheatstone bridge was employed. Soon, however, we secured from Leeds and Northrup a very fine Kohlrausch slide-wire bridge, by means of which it was possible to read to fractions of a millimeter.

The resistance box, thermometers, thermostats, and other apparatus scarcely require detailed description. In general, all the precautions were taken which Wightman and Jones recommend.

Procedure

The method of procedure for measurements at the lower temperatures has already been described in several papers from this laboratory.

But at the more elevated temperatures much less has been done. Wightman and Jones[1] have been working simultaneously with us on this problem, and their work has just been published. Clover and Jones[2] and West and Jones[3] are our only predecessors. A brief review of their work might not be out of place here.

Clover and Jones encountered a number of difficulties, in their higher temperature measurements, which had never been noticed in the lower temperature work. The cell constants changed frequently. The solubility of the glass was noticeable. The coefficient of expansion of water had to be taken into consideration. How they coped with these problems will be seen from the following quotations, taken from their paper: *Cell constants*. "It has developed that a strain is brought about by the high temperatures, which may result in a change either in the distance of the electrode plates from each other or in the surface of the plates.

"Since such a variation had not previously been observed

[1] THIS JOURNAL, **48**, 320 (1912).
[2] *Ibid.*, **43**, 187 (1910).
[3] *Ibid.*, **44**, 508 (1911).

in work covering a range from 0° to 35°, it was thought that the changes might be reduced by maintaining the cells at a temperature which was about a mean of those employed in the experimental work. Accordingly, when not in use, the cells were filled with pure water and placed in a bath which was maintained continuously at a temperature of 45° to 50°."

They then describe the following experiment:

"The measurements were first carefully made at 35° and duplicated; then the regular systematic procedure was gone through at 65°, and after this the readings at 35° were again made. If the results obtained the second time should agree with those first obtained at 35°, this would be strong evidence that the method was reliable. It was found in some cases that the second reading differed slightly from the first. In other cases there was no difference, and the change appeared to be independent of the cell used, or the concentration of the solution. It was found, further, that on standing for a considerable length of time at 35° (2 or 3 hours) *the reading slowly changed back in all cases to the original value.* It is difficult to see what other cause can be assigned to these results than a temporary change in the cell constant during the heating at 65°."

Solubility of Glass.—"In conductivity work at ordinary temperatures this factor has always been neglected, and probably is not sufficiently large to influence the results even with very dilute solutions. However, at 50° the error introduced by this factor at a dilution of 1000 is greater than any of the other ordinary experimental errors. At 65° the solubility of the glass is still greater, and at 80° the conductivity of pure water is increased tenfold on remaining in the cell for a couple of hours. In this connection it may be stated that the cells employed were made of hard glass. Of course, the amount of glass dissolved depends upon the exact nature of the latter, and was found to vary considerably with the different cells used, and at different intervals in the case of any one cell. The idea of introducing a correction for the solubility of the glass was abandoned, but the difficulty was overcome in another way. It was found that after the cells had been heated

with water for several hours the amount of glass dissolved gradually decreased and finally amounted to practically nothing. After this treatment, as the cells were kept in a bath at 45° and 50° and the water in them changed once a day, the solubility of the glass at 65° was always practically nothing, or entirely negligible. If a cell were removed from the bath and allowed to stand filled with water at room temperature for any length of time, it was found that glass was again dissolved on heating."

Because of the great increase in the coefficient of expansion of water with rising temperature, Clover and Jones found it necessary to make up the solutions at the *exact temperature* at which they were to be measured. That is, for the same acid, one set of solutions was prepared at 50° and another at 65°. The solutions prepared at the former temperature were also used for measurements at 35°, and the correction factor 0.994 was then applied.

It was found advisable nearly to fill the cells with the solution for the following reasons: "First, to minimize any slight change in concentration brought about by condensation or escape of the solvent, or from any other cause. Second, to exclude the air with its accompanying carbon dioxide from the cell, as the oxide would be dissolved during the manipulation and would influence the results with dilute solutions. Third, to prevent difficulty in opening the cells. With a large air space diminished pressure is quickly produced on removal from the bath, and if the cells can be opened at all it can be done only at the risk of distorting the electrodes."

In the following year West and Jones took up again the problem of conductivity measurements at relatively high temperatures. They found that by heating the glass vessels first with dilute sodium hydroxide, then with dilute hydrochloric acid and lastly with conductivity water, the solubility of the glass could be reduced to a negligible quantity.

They also devised the following method for determining the cell constants: "The standard solution of potassium chloride was placed in the cell. The cell was then heated to 50°, and after remaining at that temperature for about an

hour was cooled to 20°. *As soon as temperature equilibrium* was established at 20° the conductivity readings were made and the cell constants calculated." In this manner the constants of the cells, with electrodes and everything in the 50° bath, were taken at 20°, where the conductivity of the standard potassium chloride is known. Clover and Jones had previously found (as stated above) that the cells would be required to stand in a 20° bath for *several hours* before their electrodes would resume the 20° position.

Probably the most beneficial contribution that West and Jones made to this work was their method for preparing solutions. The following brief quotation explains both the method and its advantages:

"Since we worked over a range of temperature of only 30°, we found it convenient to prepare the solutions at the intermediate temperature, 50°, and then to use the solutions at the three temperatures, 35°, 50° and 65°. But since the volume of a solution varies with the temperature it was, of course, necessary to apply a correction at 35° and 65° to the volume of solutions made up at 50°.

"When a standard solution is cooled from 50° to 35° there is a contraction in volume and a subsequent increase in the concentration of the solution. The value of μ_v for any solution would, therefore, be slightly too large. The value of μ_v as found must be multiplied by the factor 0.994 for results at 35° when the solutions were made up at 50°. The correction factor for solutions made up at 50° and used at 65° is 1.0076.

"The coefficient of expansion for distilled water is somewhat less than that for an aqueous solution. However, the difference in the coefficients for water and for that of our most concentrated solution is so small that it is negligible.

"By making use of the above correction it was necessary to prepare only one set of solutions for each salt; and, consequently, much pure material and time were saved."

When we began the investigations at higher temperature these two questions presented themselves:

First. If the cells give evidence of soluble glass whenever

they are heated to 50°, cooled to room temperature and then heated to 50° again, will not the measuring flasks show this same tendency? For the measuring flasks are not kept in the heated bath, when not in use.

Second. When a solution at 50° is poured into a burette, then transferred to a measuring flask slowly, so that the burette may drain, what will be its temperature at the end of the procedure? Clearly not 50°, since a burette has a large surface in contact with the cool air of the room. And the process of draining at best must require two minutes or more. So when the experimenter imagines he is drawing off x cc. at 50°, he is actually drawing off x cc. at some lower temperature—that is, more than x cc. at 50°.

A simple device did away with both these possible sources of error. At 50°, 988.07 grams of distilled water have a volume of 1000 cc. Our liter flask was weighed at 20°. Then 988.07 grams of distilled water at 20° were introduced—air displacement being taken into account. The flask was marked at the bottom of the meniscus. This flask filled to the mark with water at 20° (room temperature) will contain a liter at 50°. Therefore, all the mother solutions could be made up for 50° work at 20°, and the solubility of the glass, which is noticeable only at higher temperatures, is thus made negligible.

This mother solution will be, let us say, normal at 50°. At 20° it is stronger than normal. If we draw out 100 cc. at 20° and dilute it to a volume of 200 cc. at 20° it will also be stronger than half normal. But heat this latter solution to 50° and it will again attain its required normality—assuming that the coefficient of expansion of water is the same as that of dilute solutions. And all solutions worked with were eighth-normal, or more dilute. This permits us to titrate all solutions at room temperature, which obviates the second of the above difficulties.

The values of the limiting conductivities (μ_∞) of the monobasic organic acids were calculated from the μ_∞ of their sodium salts. This well known method consists merely in deducting the migration velocity of the sodium ion from the value of

the sodium salt, and in substituting in its place the migration velocity of the hydrogen ion. The equation of White and Jones[1] is self-explanatory.

μ_∞ (acid) = μ_∞ (Na salt of acid)—μ_∞ (NaCl)+μ_∞ (HCl). The μ_∞ values for hydrochloric acid and sodium chloride have been determined by previous workers. The sodium salt of the acid in question was made by titration of the acid with sodium hydroxide from alcohol—phenolphthalein being used as an indicator. Only solutions of a concentration of N/2048 were used, since it was found by White and Jones[2] that the μ_∞ values of the sodium salts generally occur at this concentration.

For dibasic organic acids the μ_∞ of the sodium salt cannot be directly determined. Ostwald[3] has, however, described a satisfactory method for obtaining the value of μ_∞ for the acid. Dibasic acids, he says, in most cases dissociate like monobasic acids—setting free only one hydrogen cation. And the limiting conductivities of monobasic acids seem to be a function of the number of atoms contained in the anions. Therefore, a dibasic acid having 16 atoms should give the same μ_∞ value as a monobasic acid containing 16 atoms; and the latter value can be experimentally obtained.

The following table shows the limiting conductivities of all the acids with which we worked. These acids are arranged in the order of the number of atoms contained in their molecule. The values for the dibasic acids were worked out as described above.

The four asterisked values—pyromucic acid at 0° and 25° and sulphanilic and metanilic acids at 0°—are taken from the data of White and Jones.[4] At 35° their values coincide exactly with ours.

Dibromosuccinic and sulphosalicylic acids are omitted from the following list. As may be seen from their conductivities, they do not dissociate as monobasic acids; therefore, the method of Ostwald for finding their μ_∞ could not be employed.

[1] This Journal, **44**, 159 (1910).
[2] *Ibid*, **44**, 161 (1910).
[3] Z. physik. Chem., **1**, 74 (1887).
[4] This Journal, **44**, 163 (1910).

Acid	Atoms	*Limiting Conductivities* 0°	15°	25°	35°	50°	65°
Dichloroacetic	8	221.7	305.6	359.3	408.7	477.3	545.8
Bromosuccinic	10	222.2	302.1	354.1	...	...	...
Pyromucic	12	223.0*	...	355.0*	405.0	471.0	539.2
Salicylic	16	...	...	...	403.0	472.5	539.0
Phenylpropiolic	17	222.2	300.4	352.0	400.0	470.0	539.0
Dimethylmalonic	17	222.2	300.4	352.0	400.0	470.0	539.0
Ethylmalonic	17	222.2	300.4	352.0	400.0	470.0	539.0
o-Phthalic	18	...	...	...	400.0	470.0	538.8
Sulphanilic	18	222.0*	...	350.9	400.0	470.0	538.8
Metanilic	18	222.0*	...	350.9	400.0	470.0	538.8
Phenylacetic	18	...	...	...	400.0	466.0	535.2
Allylmalonic	18	221.4	299.3	350.9	400.0	468.0	537.0
Cinnamic	19	...	...	...	399.2	470.0	537.2
Dinitroaminophenol	19	221.7	299.1	350.2	399.0	470.0	537.2
Anisic	19	221.7	299.1	350.2	399.0	470.0	577.2
Vanillic	20	221.3	299.1	349.8	397.3	464.0	532.8
Coumaric	20	220.9	298.9	349.8	397.9	468.0	534.4
Methylethylmalonic	20	221.0	299.0	349.8	397.2	464.0	533.0
Isopropylmalonic	20	221.0	299.0	349.8	397.3	464.0	533.0
Hydrocinnamic	21	220.8	298.9	349.7	397.2	463.5	532.6
Acetylsalicylic	21	220.8	297.4	344.4	397.9	463.5	...
Diethylmalonic	23	219.4	296.1	346.2	393.2	464.8	533.9
Butylmalonic	23	219.4	296.1	346.2	393.9	464.8	533.9
Benzylmalonic	24	219.0	295.6	345.7	393.2	464.0	533.0
Napthionic	24	221.9	296.3	352.2	401.1	468.0	534.5
Dipropylmalonic	29	218.6	295.1	345.7	392.8	458.0	520.0

Measurements with bromosuccinic and acetylsalicylic acids could not be completed at higher temperatures, because these acids decomposed.

The sodium salt of dinitroaminophenol could not be made by titration, because of the depth of color of the solution.

No indicator was necessary in the case of coumaric acid—the solution itself turning green when neutralized with sodium hydroxide.

It will be seen from the above table that the values for μ_∞ decrease pretty regularly. A curve, in which the ordinates represent μ_∞ values and the abscissae the number of atoms, shows this relation very nicely. The following diagram was plotted in this manner—μ_∞ values for monobasic acids at 25° and 65° being used as examples.

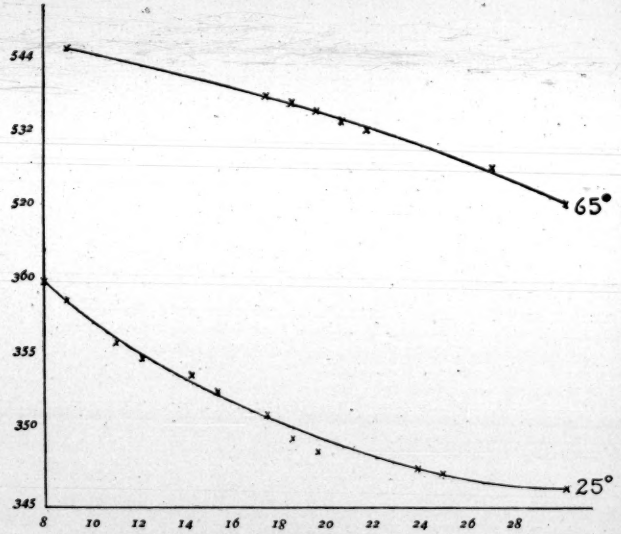

FIG. 1.—Limiting conductivities

Results

The results of our conductivity measurements are tabulated in the following pages. The molecular conductivities (μ_v) are expressed in Siemens' units.

The temperature coefficients expressed in conductivity units = $(\mu_{t_1} - \mu_t)/(t_1 - t)$.

The percentage temperature coefficients = *cond. units*$/\mu_t$ where t is the one temperature, t_1 the next higher temperature measured, μ_t and μ_{t_1} the conductivities for the same solution, measured at temperatures t and t_1, respectively.

Percentage dissociation (α) is of course μ_v/μ_∞.

The dissociation constants (K) = $\alpha^2/(1-\alpha)V$, which is the Ostwald dilution law.

Dichloroacetic Acid, $CHCl_2.COOH$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
32	166.0	220.3	253.9	286.9	330.8	356.8
128	203.7	272.6	318.0	360.4	418.3	453.3
512	220.5	300.0	352.8	403.8	468.6	528.4
1024	221.7	305.6	359.3	408.7	470.0	535.8
2048	217.0	302.1	358.1	408.5	477.3	545.8

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	3.62	3.36	3.30	2.93	1.75
128	4.59	4.54	4.24	3.86	2.33
512	5.30	5.28	5.10	4.19	3.99
1024	5.46	5.37	4.94	4.09	4.39
2048	5.67	5.60	5.04	4.59	4.57

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	2.18	1.53	1.30	1.02	0.52
128	2.25	1.66	1.33	1.07	0.56
512	2.41	1.76	1.43	1.04	0.87
1024	2.46	1.75	1.37	1.00	0.90
2048	2.61	1.85	1.41	1.12	0.95

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
32	74.87	72.09	70.67	70.20	69.32	65.37
128	91.88	89.20	88.51	88.12	87.64	83.05
512	99.46	98.17	98.18	98.80	98.18	96.81
1024	100.00	100.00	100.00	100.00	98.47	98.17
2048					100.00	100.00

Phenylacetic Acid, $C_6H_5CH_2.COOH$

Molecular Conductivity

V	35°	50°	65°
32	15.81	17.79	19.26
128	30.68	34.75	37.53
512	58.60	65.64	70.98
1024	78.80	88.31	95.18
2048	106.1	120.0	130.0

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	0.132	0.83	0.098	0.55
128	0.260	0.84	0.185	0.49
512	0.470	0.80	0.356	0.54
1024	0.634	0.80	0.451	0.51
2048	0.926	0.87	0.666	0.55

Percentage Dissociation

V	35°	50°	65°
32	3.95	3.86	3.60
128	7.72	7.46	7.01
512	14.65	14.08	13.26
1024	19.70	18.95	17.78
2048	26.53	25.75	24.29

Dissociation Constants

V	35°	50°	65°
32	0.507	0.484	0.420
128	0.505	0.470	0.413
512	0.491	0.451	0.396
1024	0.472	0.433	0.375
2048	0.468	0.436	0.381

Ethylmalonic Acid, $C_2H_5CH(COOH)_2$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
8	20.85	28.08	32.62	36.64	41.67	46.09
32	40.90	55.22	64.42	72.53	82.52	90.66
128	73.08	98.35	114.55	129.09	146.60	161.77
512	119.8	161.7	188.9	213.0	243.3	269.9
1024	146.4	197.8	231.2	260.0	297.9	330.6
2048	166.7	125.4	263.5	298.3	345.3	384.7

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
8	0.48	0.45	0.40	0.33	0.29
32	0.95	0.92	0.81	0.67	0.54
128	1.68	1.62	1.45	1.17	1.01
512	2.79	2.72	2.41	2.02	1.64
1024	3.42	3.34	2.88	2.53	2.18
2048	3.91	3.81	3.48	3.13	2.63

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
8	2.31	1.61	1.23	0.91	0.71
32	2.33	1.66	1.27	0.92	0.66
128	2.30	1.65	1.26	0.90	0.66
512	2.33	1.68	1.27	0.95	0.67
1024	2.33	1.69	1.25	0.97	0.71
2048	2.35	1.69	1.32	1.04	0.76

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
8	9.38	9.34	9.27	9.17	8.85	8.55
32	18.41	18.38	18.31	18.15	17.56	16.82
128	32.89	32.73	32.56	32.30	31.20	30.01
512	53.93	53.82	53.70	53.30	51.77	50.08
1024	65.91	65.83	65.72	65.06	63.40	61.34
2048	75.04	75.00	74.91	74.65	73.47	71.37

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
8	12.1	12.0	11.8	11.6	10.7	10.0
32	12.9	12.9	12.8	12.5	11.6	10.6
128	12.6	12.4	12.3	12.0	11.0	10.0
512	12.3	12.2	12.2	11.9	10.9	9.8
1024	12.4	12.3	12.3	11.8	10.7	9.5

Isopropylmalonic Acid, $(CH_3)_2CHCH(COOH)_2$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
32	40.07	54.69	64.92	73.63	84.05	91.73
128	72.21	98.65	117.0	132.34	151.88	168.00
512	118.6	161.6	192.9	217.6	248.8	278.4
1024	144.1	197.0	234.0	264.4	307.7	343.8
2048	167.4	228.9	272.2	307.9	357.0	402.5

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	0.97	1.02	0.87	0.69	0.51
128	1.76	1.83	1.53	1.30	1.07
512	2.86	3.14	2.47	2.08	1.97
1024	3.53	3.70	3.04	2.89	2.41
2048	4.10	4.32	3.77	3.27	3.03

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	2.43	1.87	1.34	0.94	0.61
128	2.43	1.86	1.31	0.98	0.71
512	2.41	1.88	1.28	0.96	0.79
1024	2.45	1.88	1.30	0.92	0.78
2048	2.45	1.88	1.38	1.06	0.85

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
32	18.14	18.29	18.56	18.50	18.11	17.21
128	32.69	33.00	33.45	33.26	32.73	31.52
512	53.70	54.04	55.15	54.69	53.62	53.23
1024	65.24	65.89	66.89	66.44	66.31	64.50
2048	75.79	76.59	77.80	77.30	76.94	75.51

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
32	12.5	12.8	13.2	13.1	12.5	11.2
128	12.4	12.7	13.1	12.9	12.5	11.3
512	12.2	12.4	13.2	12.9	12.1	11.2
1024	12.0	12.4	13.2	12.8	12.5	11.4
2048	11.6	12.2	13.3	12.9	12.5	11.3

Butylmalonic Acid, $C_4H_9CH(COOH)_2$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
32	37.53	50.60	58.72	66.30	76.00	83.93
128	68.80	92.04	107.34	121.86	141.00	156.00
512	113.8	154.20	180.9	204.8	236.2	264.2
1024	140.0	187.2	218.3	248.0	286.2	320.1
2048	163.7	218.8	255.4	291.3	340.0	382.6

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	0.87	0.81	0.78	0.65	0.53
128	1.55	1.53	1.45	1.28	1.00
512	2.69	2.67	2.39	2.09	1.87
1024	3.15	3.11	2.97	2.55	2.26
2048	3.67	3.66	3.59	3.25	2.84

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	2.32	1.60	1.32	0.98	0.69
128	2.25	1.66	1.35	1.04	0.71
512	2.36	1.73	1.32	1.02	0.79
1024	2.25	1.66	1.36	1.02	0.79
2048	2.23	1.67	1.40	1.11	0.83

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
32	17.11	17.09	16.96	16.83	16.35	15.71
128	31.36	31.08	31.00	30.92	30.35	29.21
512	51.88	52.08	52.25	52.00	50.82	49.48
1024	63.82	63.22	63.05	62.96	61.57	60.00
2048	74.62	73.89	73.48	73.95	73.15	71.65

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
32	11.0	11.0	10.8	10.6	10.0	9.15
128	11.2	11.0	10.9	10.8	10.3	9.4
512	10.9	11.0	11.1	11.0	10.2	9.5
1024	11.0	10.6	10.5	10.4	9.6	8.8
2048	10.7	10.2	10.0	10.3	9.7	8.8

Allylmalonic Acid, $CH_2 : CHCH_2CH(COOH)_2$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
8	24.25	32.63	37.73	42.26	48.94	53.61
32	45.62	61.58	71.47	80.30	92.02	101.16
128	80.81	109.08	126.33	142.15	164.78	181.65
512	130.5	176.3	204.4	231.0	264.5	293.2
1024	158.9	214.0	248.7	281.0	322.7	358.3
2048	176.4	237.9	277.4	313.8	358.6	401.5

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
8	0.56	0.51	0.45	0.44	0.31
32	1.06	0.99	0.88	0.78	0.61
128	1.88	1.72	1.58	1.51	1.12
512	3.05	2.81	2.66	2.23	1.92
1024	3.67	3.47	3.23	2.78	2.37
2048	4.10	3.95	3.64	2.98	2.86

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
8	2.30	1.56	1.20	1.05	0.63
32	2.33	1.60	1.23	0.98	0.66
128	2.33	1.58	1.25	1.06	0.68
512	2.33	1.59	1.30	0.97	0.72
1024	2.31	1.62	1.30	0.99	0.73
2048	2.32	1.66	1.31	0.95	0.79

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
8	10.95	10.90	10.76	10.56	10.46	9.98
32	20.60	20.57	20.37	20.07	19.66	18.84
128	36.49	36.43	36.01	35.54	35.21	33.82
512	58.93	58.87	58.26	57.75	56.52	54.61
1024	71.77	71.47	70.89	70.25	68.96	66.72
2048	79.65	79.45	79.08	78.46	76.62	74.77

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
8	16.8	16.6	16.2	15.6	15.3	13.8
32	16.7	16.6	16.2	15.7	15.0	13.7
128	16.4	16.3	15.8	15.3	14.9	13.5
512	16.5	16.5	15.9	15.4	14.4	12.8
1024	....	....	....	....	14.9	13.1

Benzylmalonic Acid, $C_6H_5CH_2CH(COOH)_2$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
32	45.06	60.54	69.82	78.31	89.05	97.76
128	80.22	107.44	124.99	140.37	160.03	175.82
512	128.3	171.8	199.6	225.1	259.0	285.8
1024	153.0	205.6	239.4	269.6	310.8	345.3
2048	177.7	236.2	273.7	310.0	357.9	395.3

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	1.03	0.93	0.85	0.72	0.57
128	1.81	1.75	1.54	1.31	1.05
512	2.90	2.78	2.55	2.26	1.79
1024	3.50	3.38	3.02	2.74	2.30
2048	3.89	3.85	3.64	3.19	2.49

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	2.29	1.53	1.22	0.91	0.65
128	2.20	1.57	1.23	0.93	0.66
512	2.29	1.61	1.27	1.00	0.69
1024	2.29	1.64	1.26	1.02	0.74
2048	2.19	1.63	1.32	1.04	0.69

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
32	20.57	20.48	20.19	19.91	19.18	18.33
128	36.63	36.34	36.16	35.70	34.49	32.98
512	58.58	58.11	57.74	57.24	55.81	53.62
1024	69.88	69.56	69.26	68.57	66.98	64.79
2048	81.16	79.89	79.16	78.86	77.14	74.16

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
32	16.6	16.5	16.0	15.5	14.2	12.8
128	16.5	16.2	16.0	15.5	14.1	12.7
512	16.2	15.7	15.4	15.0	13.8	12.1
1024	15.8	15.5	15.2	14.6	13.3	11.7
2048	17.0	15.5	14.7	14.4	12.7	10.4

Dimethylmalonic Acid, $(CH_3)_2C(COOH)_2$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
8	16.08	22.06	25.83	29.27	34.10	38.13
32	32.00	43.76	51.23	58.41	68.80	77.10
128	59.00	80.57	94.61	107.29	124.82	139.53
512	101.4	136.9	160.2	182.5	217.2	240.7
1024	124.1	169.7	198.9	226.0	266.7	299.3
2048	151.9	205.7	241.1	273.7	314.71	349.5

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
8	0.40	0.38	0.34	0.32	0.27
32	0.78	0.75	0.72	0.69	0.55
128	1.44	1.40	1.27	1.17	0.98
512	2.37	2.33	2.22	2.13	1.57
1024	3.04	2.92	2.71	2.71	2.17
2048	3.59	3.54	3.26	2.74	2.32

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
8	2.44	1.70	1.34	1.08	0.79
32	2.43	1.70	1.40	1.18	0.80
128	2.42	1.74	1.34	1.09	0.79
512	2.33	1.70	1.38	1.17	0.72
1024	2.45	1.72	1.36	1.18	0.82
2048	2.36	1.72	1.35	1.00	0.74

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
8	7.24	7.35	7.34	7.32	7.25	7.07
32	14.40	14.59	14.56	14.62	14.63	14.30
128	26.55	26.86	26.89	26.85	26.56	25.88
512	45.64	45.65	45.56	45.66	46.17	44.66
1024	55.85	56.58	56.55	56.56	56.72	55.52
2048	68.36	68.57	68.53	68.48	67.00	64.85

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
8	7.06	7.28	7.27	7.27	7.08	6.72
32	7.57	7.79	7.75	7.82	7.82	7.45
128	7.50	7.71	7.73	7.70	7.51	7.06
512	7.48	7.49	7.45	7.50	7.69	7.04
1024	6.90	7.20	7.21	7.20	7.26	6.77
2048	7.21	7.30	7.29	7.28	6.64	5.84

Methylethylmalonic Acid, $CH_3(C_2H_5)C(COOH)_2$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
8	23.60	31.90	37.34	42.22	48.28	54.11
32	45.89	61.89	72.45	82.00	93.61	104.35
128	81.39	110.44	129.71	147.18	168.51	188.20
512	129.9	176.0	206.3	234.0	269.5	304.3
1024	156.2	211.2	248.2	280.0	323.2	365.5
2048	178.2	240.3	280.6	315.1	365.5	411.6

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
8	0.55	0.54	0.49	0.40	0.39
32	1.07	1.06	0.95	0.77	0.72
128	1.94	1.93	1.75	1.42	1.31
512	3.07	3.04	2.77	2.37	2.32
1024	3.67	3.69	3.18	2.88	2.82
2048	4.14	4.03	3.44	3.36	3.07

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
8	2.34	1.70	1.30	0.96	0.72
32	2.33	1.71	1.31	0.94	0.76
128	2.38	1.74	1.34	0.96	0.77
512	2.36	1.72	1.34	1.01	0.85
1024	2.35	1.75	1.28	1.02	0.87
2048	2.32	1.70	1.23	1.07	0.83

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
8	10.68	10.67	10.67	10.61	10.39	10.15
31	20.78	20.70	20.71	20.61	20.17	19.58
128	36.85	36.94	37.08	36.99	36.31	35.31
512	58.84	58.85	58.99	58.81	59.08	57.08
1024	70.73	70.66	70.96	70.37	69.65	68.58
2048	80.68	80.38	80.25	79.18	78.76	77.22

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
8	16.0	15.9	15.9	15.7	15.6	14.3
32	17.0	16.9	16.9	16.7	15.9	14.5
128	16.8	16.9	17.1	17.0	16.1	15.0
512	16.4	16.4	16.6	16.4	15.7	14.8
1024	16.7	16.6	16.9	16.3	15.6	14.6
2048	16.5	16.1	15.9	15.0	14.3	12.8

Diethylmalonic Acid, $(C_2H_5)_2C(COOH)_2$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
8	52.38	67.87	76.92	84.66	94.03	100.32
32	92.77	121.64	138.84	153.60	174.26	186.22
128	141.8	187.3	215.3	240.2	275.0	299.0
512	189.0	252.3	292.2	328.7	378.8	422.6
1024	201.2	268.2	312.0	353.6	413.7	462.8
2048	201.6	272.2	317.2	360.5	424.4	471.6

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
8	1.03	0.90	0.77	0.72	0.42
32	1.92	1.72	1.48	1.38	0.80
128	3.04	2.80	2.49	2.33	1.67
512	4.22	3.99	3.65	3.34	2.92
1024	4.47	4.37	4.16	4.01	3.27
2048	4.71	4.50	4.32	4.26	3.83

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50	50°–65°
8	1.97	1.33	1.00	0.85	0.44
32	2.07	1.41	1.06	0.89	0.46
128	2.14	1.49	1.15	0.97	0.61
512	2.23	1.58	1.25	1.01	0.77
1024	2.22	1.63	1.33	1.13	0.79
2048	2.33	1.65	1.36	1.18	0.90

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
8	23.88	22.92	22.22	21.49	20.23	18.79
32	42.29	41.08	40.10	39.00	37.49	34.87
128	64.65	63.27	62.19	60.98	59.15	56.00
512	86.17	85.21	84.40	83.46	81.56	79.14
1024	91.73	90.59	90.10	89.76	89.00	86.66
2048	91.92	91.94	91.62	91.52	91.30	88.32

Dipropylmalonic Acid, $(C_3H_7)_2C(COOH)_2$
Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
32	103.2	135.1	154.5	170.3	...	...
128	152.2	204.4	234.9	261.7	297.5	304.2
512	192.1	258.8	300.6	339.3	386.5	430.1
1024	203.5	272.9	317.8	359.1	417.0	468.0
2048	209.3	281.1	328.9	373.0	434.6	490.9

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	2.13	1.94	1.58	....	....
128	3.47	3.06	2.68	2.39	1.78
512	4.45	4.18	3.86	3.15	2.95
1024	4.63	4.49	4.14	3.86	3.40
2048	4.78	4.78	4.41	4.11	3.75

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	2.06	1.41	1.02	....	....
128	2.28	1.49	1.14	0.91	0.60
512	2.31	1.62	1.28	0.93	0.74
1024	2.27	1.64	1.30	1.09	0.81
2048	2.29	1.70	1.34	1.10	0.86

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
32	47.18	45.78	44.70	43.35	...	...
128	69.63	69.25	67.95	66.60	64.96	62.34
512	87.85	87.70	86.97	86.35	84.40	82.77
1024	93.07	92.48	91.92	91.41	91.06	90.00
2048	95.74	95.26	95.15	94.93	94.89	94.40

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
32	132	121	113	104	..	..
128	125	121	113	104	90	81
512	124	122	113	106	89	78
1024	122	111	102	95	90	79
2048	105	93	91	90	90	78

Bromosuccinic Acid, $HOOCCHBrCH_2COOH$

Molecular Conductivity

V	0°	15°	25°
128	101.46	136.01	158.19
512	156.00	210.27	246.72
1024	189.44	252.44	293.74
2048	208.37	283.02	328.50

Temperature Coefficients

	0°–15°		15°–25°	
V	Cond units.	Per cent.	Cond units.	Per cent.
128	2.30	2.27	2.21	1.60
512	3.62	2.32	3.60	1.62
1024	4.20	2.22	4.13	1.60
2048	4.71	2.26	4.55	1.61

Percentage Dissociation

V	0°	15°	25°
128	45.66	45.02	44.67
512	70.20	70.40	69.66
1024	85.25	83.55	82.94
2048	93.77	93.67	92.76

Dissociation Constants

V	0°	15°	25°
128	30	29	28
512	32	33	31
1024	48	41	39
2048	69	68	58

Dibromosuccinic Acid, HOOCCHBrCHBrCOOH

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
32	175.6	222.2	245.6	262.9	293.4	342.6
128	254.3	326.8	367.6	399.7	448.6	509.8
512	339.1	438.4	497.4	546.5	615.0	685.9
1024	381.6	501.8	571.4	635.0	707.1	786.1
2048	416.1	550.0	631.9	704.9	792.2	879.4

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	3.10	2.34	1.74	2.03	3.28
128	4.83	4.07	3.21	3.26	4.08
512	6.62	5.99	4.91	4.56	4.73
1024	8.01	6.96	6.35	4.81	5.26
2048	8.92	8.19	7.39	5.82	5.82

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	1.77	1.05	0.71	0.77	1.09
128	1.89	1.24	0.87	0.82	0.91
512	1.95	1.34	0.98	0.83	0.77
1024	2.10	1.39	1.11	0.76	0.74
2048	2.14	1.49	1.15	0.83	0.73

Pyromucic Acid, C_4H_3OCOOH

Molecular Conductivity

V	35°	50°	65°
8	28.59	31.59	33.36
32	56.36	62.36	66.56
128	105.01	116.32	124.38
512	179.4	199.9	213.8
1024	223.0	249.2	265.3
2048	269.2	308.9	333.9

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
8	0.20	0.70	0.12	0.37
32	0.40	0.71	0.28	0.45
128	0.75	0.72	0.54	0.46
512	1.37	0.76	0.93	0.46
1024	1.78	0.79	1.07	0.43
2048	2.65	0.98	1.67	0.54

Percentage Dissociation

V	35°	50°	65°
8	7.07	6.71	6.19
32	13.93	13.24	12.34
128	25.96	24.69	23.07
512	44.35	42.44	39.65
1024	55.13	52.91	49.20
2048	66.55	65.58	61.93

Dissociation Constants

V	35°	50°	65°
8	6.7	6.0	5.1
23	7.0	6.3	5.4
128	7.1	6.3	5.4
512	6.9	6.1	5.1
1024	6.6	5.8	4.8
2048	6.5	6.1	4.9

Phenylpropiolic Acid, $C_6H_5C \vdots CCOOH$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
128	132.6	177.0	203.3	227.2	255.6	274.7
256	154.8	208.0	239.2	267.6	301.2	327.4
512	176.1	236.6	274.4	307.8	349.7	375.3
1024	191.4	258.0	299.8	339.2	392.1	422.1
2048	200.5	269.0	314.8	357.9	416.6	449.6

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
128	2.96	2.63	2.39	1.89	1.27
256	3.54	3.12	2.84	2.24	1.53
512	4.05	3.78	3.34	2.77	1.71
1024	4.44	4.08	3.94	3.53	2.00
2048	4.56	4.58	4.31	3.91	2.20

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
128	2.23	1.48	1.17	0.83	0.50
256	2.24	1.50	1.18	0.84	0.51
512	2.25	1.59	1.21	0.90	0.49
1024	2.32	1.62	1.31	1.04	0.51
2048	2.27	1.70	1.36	1.09	0.53

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
128	59.67	58.91	57.87	56.82	54.39	50.98
256	69.66	69.22	68.08	66.90	64.09	60.76
512	79.24	78.76	78.12	76.97	74.41	69.66
1024	86.15	85.89	85.34	84.81	83.43	78.35
2048	90.25	89.54	89.60	89.48	88.63	83.43

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
128	68.9	66.0	62.1	58.4	50.7	41.4
256	62.5	60.8	56.7	52.8	44.7	36.8
512	59.1	57.0	54.5	50.2	42.3	31.2
1024	52.3	51.1	48.5	46.2	41.0	27.7
2048	40.8	37.4	37.7	37.2	33.7	20.5

Salicylic Acid, HOC_6H_4COOH

Molecular Conductivity

V	35°	50°	65°
64	93.64	110.55	124.60
128	125.96	148.72	166.80
512	209.7	249.1	280.1
1024	255.0	301.7	337.2
2048	294.6	350.1	392.6

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
64	1.13	1.21	0.94	0.85
128	1.52	1.21	1.20	0.81
512	2.63	1.25	2.07	0.83
1024	3.11	1.22	2.37	0.79
2048	3.70	1.25	2.77	0.79

Percentage Dissociation

V	35°	50°	65°
64	23.24	23.37	23.13
128	31.26	31.44	30.96
512	52.05	52.67	52.00
1024	63.29	63.78	62.58
2048	73.12	74.01	72.87

Dissociation Constants

V	35°	50°	65°
64	11.0	11.1	10.9
128	11.1	11.2	10.8
512	11.0	11.4	11.0
1024	10.7	11.0	10.2

Acetylsalicylic Acid, $CH_3COOC_6H_4COOH$

Molecular Conductivity

V	0°	15°	25°	35°	50°
128	40.40	52.78	60.60	68.89	79.41
512	73.10	95.21	109.27	124.34	142.88
1024	92.60	121.0	139.3	158.7	184.1
2048	118.1	154.5	177.6	205.1	238.3

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°
128	0.83	0.78	0.83	0.70
512	1.47	1.41	1.51	1.24
1024	1.89	1.83	1.94	1.69
2048	2.43	2.30	2.75	2.35

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°
128	2.04	1.48	1.37	1.02
512	2.01	1.48	1.38	1.00
1024	2.04	1.51	1.39	1.06
2048	2.14	1.49	1.54	1.14

Percentage Dissociation

V	0°	15°	25°	35°	50°
128	18.30	17.75	17.59	17.31	17.13
512	33.11	32.00	31.73	31.25	30.82
1024	41.49	40.68	40.45	39.89	39.72
2048	53.50	51.95	51.55	51.54	51.42

Dissociation Constants

V	0°	15°	25°	35°	50°
128	3 2	3.0	2.9	2.8	2.7
512	3.2	2.9	2.9	2.8	2.7
1024	3.0	2.7	2.7	2.6	2.6
2048	3.0	2.7	2.7	2.7	2.7

Sulphosalicylic Acid, $HOC_6H_3(SO_3H)COOH$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
32	209.4	283.7	332.0	377.6	432.9	486.8
128	239.6	328.5	386.5	440.1	508.9	575.4
512	291.9	403.3	474.1	538.5	622.4	706.2
1024	322.5	443.0	522.4	598.1	701.3	785.7
2048	352.0	485.0	570.4	651.7	762.3	858.0

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	4.95	4.83	4.56	3.69	3.59
128	5.93	5.79	5.36	4.61	4.43
512	7.42	7.08	6.44	5.59	5.58
1024	8.04	7.93	7.57	6.84	5.62
2048	8.87	8.54	8.13	7.38	6.38

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	2.36	1.70	1.37	0.98	0.83
128	2.47	1.76	1.38	1.05	0.87
512	2.54	1.75	1.35	1.04	0.89
1024	2.49	1.79	1.44	1.14	0.81
2048	2.51	1.76	1.42	1.13	0.84

Anisic Acid, $CH_3OC_6H_4COOH$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
1024	35.80	50.50	59.10	67.60	80.29	90.25
2048	47.13	66.74	78.80	90.15	103.67	115.17

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
1024	0.98	0.86	0.85	0.84	0.66
2048	1.31	1.20	1.13	0.90	0.77

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
1024	2.74	1.70	1.43	1.24	0.82
2048	2.77	1.80	1.43	1.00	0.74

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
1024	16.14	16.84	16.88	16.94	17.06	16.80
2048	21.26	22.25	22.50	22.59	22.03	21.44

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
1024	0.303	0.333	0.335	0.337	0.343	0.331
2048	0.280	0.311	0.319	0.322	0.304	0.285

Vanillic Acid, $CH_3OC_6H_3(OH)COOH$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
256	18.48	26.44	31.68	36.49	42.32	47.41
512	26.16	36.65	43.30	49.89	57.80	64.62
1024	35.87	50.10	59.55	69.00	80.38	89.42
2048	47.26	67.40	80.88	93.48	109.15	120.08

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
256	0.53	0.52	0.48	0.39	0.34
512	0.70	0.66	0.66	0.53	0.45
1024	0.95	0.95	0.94	0.76	0.60
2048	1.34	1.34	1.26	1.04	0.73

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
256	2.87	1.98	1.52	1.07	0.80
512	2.67	1.81	1.52	1.06	0.79
1024	2.63	1.88	1.58	1.10	0.75
2048	2.80	1.99	1.55	1.11	0.67

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
256	8.35	8.84	9.05	9.18	9.12	8.90
512	11.82	12.25	12.38	12.56	12.46	12.13
1024	16.21	16.75	17.33	17.37	17.32	16.78
2048	21.35	22.53	23.12	23.53	23.52	22.54

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
256	0.30	0.33	0.35	0.36	0.36	0.34
512	0.31	0.33	0.34	0.35	0.35	0.33
1024	0.31	0.33	0.35	0.36	0.35	0.33
2048	0.28	0.32	0.34	0.35	0.35	0.32

Metanilic Acid, $H_2NC_6H_4SO_3H$

Molecular Conductivity

V	35°	50°	65°
32	35.37	49.48	66.05
128	66.86	92.74	123.89
512	122.35	165.15	216.84
1024	158.2	210.0	267.3
2048	202.4	264.3	331.7

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
32	0.94	2.66	1.10	2.23
128	1.72	2.57	2.08	2.24
512	2.85	2.33	3.44	2.09
1024	3.45	2.18	3.82	1.81
2048	4.13	2.04	4.49	1.63

Percentage Dissociation

V	35°	50°	65°
32	8.84	10.53	12.25
128	16.72	19.73	22.99
512	30.58	35.14	40.24
1024	39.55	44.68	49.61
2048	50.60	56.23	61.56

Dissociation Constants

V	35°	50°	65°
32	2.68	3.87	5.34
128	2.62	3.80	5.36
512	2.63	3.72	5.29
1024	2.53	3.52	4.79
2048	2.53	3.53	4.81

Sulphanilic Acid, $H_2NC_6H_4SO_3H$

Molecular Conductivity

V	25°	35°	50°	65°
32	45.39	58.35	78.23	100.50
128	85.40	107.80	145.00	186.40
512	148.66	180.88	237.00	298.00
1024	182.8	221.6	287.0	352.6
2048	223.0	268.0	336.8	406.7

Temperature Coefficients (Cond. Units)

	25°–35°		35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
32	1.30	2.68	1.33	2.28	1.48	1.89
128	2.24	2.62	2.48	2.30	2.73	1.88
512	3.22	2.17	3.73	2.06	4.07	1.72
1024	3.88	2.12	4.36	1.97	4.37	1.52
2048	4.50	2.02	4.58	1.71	4.66	1.38

Percentage Dissociation

V	25°	35°	50°	65°
32	12.94	14.59	16.64	18.65
128	24.34	26.95	30.85	34.59
512	41.79	45.22	50.42	55.30
1024	52.08	55.40	61.06	65.44
2048	63.52	67.00	71.65	75.48

Dissociation Constants

V	25°	35°	50°	65°
32	6.01	7.78	10.4	13.4
128	6.09	7.77	10.7	14.2
512	5.86	7.30	10.0	13.4
1024	5.53	6.72	9.35	12.1
2048	5.40	6.64	8.84	11.3

4,6-Dinitro-2-aminophenol, $(O_2N)_2C_6H_2(NH_2)OH$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
512	24.00	39.78	51.80	64.93	85.67	110.8
1024	32.90	54.09	70.16	88.60	119.00	153.5
2048	44.60	73.80	95.20	119.7	161.8	208.4

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
512	1.05	1.20	1.31	1.38	1.67
1024	1.41	1.61	1.84	2.02	2.30
2048	1.95	2.26	2.45	2.80	3.11

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
512	4.37	3.02	2.53	2.12	1.94
1024	4.30	2.97	2.58	2.28	1.93
2048	4.37	3.10	2.57	2.34	1.92

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
512	10.82	13.30	14.73	16.27	18.22	20.62
1024	14.84	18.08	19.95	22.20	25.32	28.57
2048	20.10	24.61	27.20	29.93	34.42	38.79

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
512	0.256	0.398	0.497	0.617	0.793	1.05
1024	0.253	0.389	0.486	0.619	0.838	1.11
2048	0.247	0.392	0.496	0.624	0.882	1.20

Hydrocinnamic Acid, $C_6H_5CH_2CH_2COOH$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
32	5.89	8.07	9.40	10.57	11.81	13.00
128	11.49	15.64	18.32	20.56	23.20	25.28
512	22.18	30.46	35.49	39.85	44.82	49.00
1024	30.40	41.76	48.84	54.79	61.37	67.04
2048	41.60	56.41	65.65	73.72	83.02	89.66

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	0.145	0.133	0.104	0.083	0.079
128	0.276	0.268	0.224	0.176	0.138
512	0.552	0.503	0.436	0.331	0.278
1024	0.757	0.708	0.595	0.438	0.378
2048	0.987	0.923	0.807	0.620	0.443

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
32	2.47	1.65	1.24	0.78	0.67
128	2.41	1.71	1.22	0.85	0.59
512	2.49	1.65	1.23	0.83	0.62
1024	2.49	1.69	1.22	0.80	0.61
2048	2.37	1.64	1.23	0.84	0.53

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
32	2.67	2.70	2.69	2.66	2.55	2.44
128	5.20	5.23	5.23	5.17	5.01	4.75
512	10.04	10.17	10.14	10.03	9.67	9.20
1024	13.76	13.97	13.96	13.79	13.24	12.59
2048	18.84	18.87	18.77	18.56	17.91	16.83

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
32	0.229	0.234	0.232	0.227	0.208	0.191
128	0.223	0.225	0.225	0.220	0.206	0.185
512	0.219	0.225	0.223	0.218	0.202	0.182
1024	0.214	0.222	0.221	0.215	0.197	0.177
2048	0.214	0.214	0.212	0.205	0.191	0.166

Cinnamic Acid, $C_6H_5CH : CHCOOH$

Molecular Conductivity

V	35°	50°	65°
512	51.10	59.90	67.02
1024	69.40	80.93	90.20
2048	95.25	111.00	124.00

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
512	0.58	1.13	0.47	0.79
1024	0.77	1.11	0.62	0.77
2048	1.05	1.10	0.87	0.78

Percentage Dissociation

V	35°	50°	65°
512	12.80	12.74	12.48
1024	17.38	17.22	16.79
2048	23.86	23.62	23.08

Dissociation Constants

V	35°	50°	65°
512	0.367	0.363	0.347
1024	0.357	0.350	0.331
2048	0.365	0.357	0.338

o-Coumaric Acid, $HOC_6H_4CH : CHCOOH$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
256	16.00	23.22	27.08	30.38	35.56	39.39
512	22.40	32.39	37.58	42.01	49.08	54.24
1024	31.48	46.00	53.38	59.52	69.57	76.92
2048	44.53	65.13	75.56	77.50	90.50	98.75

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
256	0.48	0.38	0.33	0.34	0.25
512	0.67	0.52	0.44	0.47	0.34
1024	0.97	0.74	0.61	0.67	0.49
2048	1.38	1.04	0.19	0.87	0.55

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
256	3.00	1.64	1.21	1.13	0.71
512	2.99	1.61	1.18	1.12	0.70
1024	3.07	1.63	1.15	1.12	0.70
2048	3.08	1.60	0.25	1.12	0.61

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
256	7.27	7.74	7.73	7.60	7.59	7.37
512	10.18	10.80	10.74	10.51	10.48	10.15
1024	14.30	15.34	15.25	14.89	14.86	14.39
2048	20.23	21.72	21.59	19.39	19.34	18.48

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
256	0.223	0.254	0.253	0.244	0.243	0.229
512	0.225	0.255	0.252	0.241	0.240	0.224
1024	0.233	0.271	0.268	0.254	0.252	0.236
2048	0.250	0.294	0.290	0.228	0.226	0.205

o-*Phthalic Acid*, $C_6H_4(COOH)_2$

Molecular Conductivity

V	35°	50°	65°
64	96.31	110.20	122.70
128	128.06	147.58	163.86
512	212.8	244.8	272.4
1024	258.5	300.3	336.9
2048	302.7	352.7	395.1

Temperature Coefficients

	35°–50°		50°–65°	
V	Cond. units	Per cent.	Cond. units	Per cent.
64	0.93	0.96	0.83	0.75
128	1.30	1.02	1.09	0.74
512	2.13	1.01	1.84	0.75
1024	2.78	1.08	2.44	0.81
2048	3.33	1.10	2.83	0.80

Percentage Dissociation

V	35°	50°	65°
64	24.08	23.45	22.77
128	32.01	31.40	30.41
512	53.20	52.09	50.55
1024	64.62	63.89	62.53
2048	75.68	75.04	73.33

Dissociation Constants

V	35°	50°	65°
64	11.9	11.2	10.5
128	11.8	11.2	10.4
512	11.8	11.1	10.1
1024	11.5	11.0	10.2
2048	11.5	11.0	9.8

Naphthionic Acid, $C_{10}H_6(NH_2)SO_3H$

Molecular Conductivity

V	0°	15°	25°	35°	50°	65°
1024	142.2	212.7	262.0	312.9	382.6	450.6
2048	169.8	245.5	295.4	347.2	420.9	491.2

Temperature Coefficients (Cond. Units)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
1024	4.70	4.93	5.09	4.64	4.56
2048	5.05	4.99	5.16	4.92	4.68

Temperature Coefficients (Per cent.)

V	0°–15°	15°–25°	25°–35°	35°–50°	50°–65°
1024	3.30	2.32	1.94	1.48	1.19
2048	3.00	2.03	1.48	1.42	1.11

Percentage Dissociation

V	0°	15°	25°	35°	50°	65°
1024	64.04	71.82	74.43	78.23	81.75	84.29
2048	76.58	82.98	83.92	86.80	89.94	91.90

Dissociation Constants

V	0°	15°	25°	35°	50°	65°
1024	11.1	17.9	21.2	27.4	35.8	44.2
2048	12.2	19.7	21.4	27.9	39.3	50.9

The conductivities of bromosuccinic and acetylsalicylic acids could not be measured at higher temperatures. Both acids showed marked evidence of decomposition.

The time factor for the decomposition of bromosuccinic acid is striking.

V	Time	μ_v 35°
1024	30 minutes	442
	45 minutes	458
	1 hour	466
	1.5 hours	472

Acetylsalicylic acid in all probability gives salicylic and acetic acids as a result of hydrolysis:

$$C_6H_4\begin{matrix}OOCCH_3\\COOH\end{matrix} + H_2O = C_6H_4\begin{matrix}OH\\COOH\end{matrix} + CH_3COOH$$

The velocity of this reaction may be observed in the following data:

V	Time	μ_v 65°
128	35 minutes	93.8
	45 minutes	94.9
	1 hour, 10 minutes	97.3
	2 hours, 15 minutes	105.8
	3 hours	111.0

Possibly the weakening action of the substituting acetyl group in this acid finds its explanation here. We would expect acetylsalicylic acid, under ordinary conditions, to be stronger than salicylic acid. The acetyl derivatives of propionic[1] and aminobenzoic[2] acids are stronger than the original unsubstituted acids. Since, however, acetylsalicylic acid shows such marked evidence of hydrolysis, we think it fair to assume that its small conductivity is due to its great hydrating power.

The μ_∞ values for sulphosalicylic and dibromosucccinic acids, as has already been explained in connection with the table of limiting conductivities, could not be calculated. Therefore, the percentage dissociation and dissociation constants of these acids are not given.

The case of diethylmalonic acid is exceptional. The molecular conductivities at $V = 1024$ and $V = 2048$ are so nearly

[1] This Journal, **46**, 78.
[2] Z. physik. Chem., **3**, 263.

Dissociation Constants, $K \times 10^4$

Acid	0°	15°	25°	35°	50°	65°
Phenylacetic	0.540[1]	....	0.545[1]	0.506	0.477	0.416
Ethylmalonic	12.5	12.4	12.3	11.9	11.0	10.0
Isopropylmalonic	12.3	12.5	13.2	12.9	12.5	11.3
Butylmalonic	11.0	10.9	10.8	10.6	10.2	9.4
Allylmalonic	16.6	16.5	16.0	15.5	14.9	13.4
Benzylmalonic	16.4	15.9	15.0	15.0	13.6	12.0
Diethylmalonic	7.29	7.46	7.45	7.46	7.33	7.01
Methylethylmalonic	16.6	16.5	16.5	16.2	15.8	14.6
Diethylmalonic	88.0	80.0	74.0	69.0	60.0	50.0
Dipropylmalonic	124.0	121.0	113.0	104.0	90.0	79.0
Pyromucic	8.7[1]	....	7.6[1]	6.8	6.1	5.1
Salicylic	8.3[1]	....	10.6[1]	10.9	11.2	10.7
Acetylsalicylic	3.10	2.82	2.80	2.72	2.67	....
Anisic	0.291	0.322	0.327	0.330	0.324	0.308
Vanillic	0.300	0.330	0.345	0.355	0.353	0.330
Metanilic	0.90[1]	....	1.99[1]	2.64	3.80	5.33
Sulphanilic	3.28[1]	....	6.05	7.77	10.4	13.4
Dinitroaminophenol	0.252	0.393	0.493	0.62	0.84	1.12
Hydrocinnamic	0.220	0.224	0.223	0.217	0.206	0.186
Cinnamic	0.322[1]	....	0.368[1]	0.363	0.357	0.339
Coumaric	0.233	0.269	0.266	0.242	0.240	0.224
Phthalic	13.4[1]	....	12.6[1]	11.7	11.1	10.2
Naphthionic	11.7	18.8	21.3	27.6	37.5	47.5

[1] These constants at lower temperatures were calculated by White and Jones: THIS JOURNAL, **44**, 159 (1910).

alike that we might imagine the acid to be almost completely dissociated at these dilutions. Calculated in the usual manner, however, the μ_∞ values do not agree with these. Take for example, μ_∞ at 0° for an acid with 23 atoms, $\mu_\infty = 219.4$. In the case of diethylmalonic acid the experimentally obtained $\mu_\infty = 201.6$. Dissociation constants calculated on the basis of the theoretical μ_∞ scarcely deserve the name of "constants," and are, therefore, omitted from our list.

Owing to the fact that the Ostwald dilution law does not hold for strong acids, many "dissociation constants" belonging to acids of this class are omitted. Some that are given are extremely irregular, and are only of value inasmuch as they indicate the relative strengths of the acids.

In the above table are the probable dissociation constants of most of the acids with which we worked.

Several investigators, who had not made measurements at such high temperatures, observed that while most of the percentage dissociations of organic acids decreased with rising temperature, some of them persistently increased. This increase, however, continued at a diminishing rate. The maximum dissociation has been reached in our work in every case except for the amino acids—sulphanilic, metanilic, naphthionic, dinitroaminophenol. The next class of acids for which the dissociation increased over a wide range in temperature were those acids related to hydroxybenzoic—salicylic, anisic and vanillic acids. These attained maximum dissociation at 35°.

The above mentioned amino acids conform to the observations of White and Jones. Their percentage temperature coefficients of conductivity are exceptionally large, and the coefficients expressed in conductivity units increase with rise in temperature. The dissociation constants of dinitroaminophenol and naphthionic acid also increase slightly with dilution. Ostwald[1] has accounted for all of these facts by assuming that at low temperatures and high concentration these amino acids form inner salts, which break down on raising the temperature or the dilution, or both, yielding the free acid. This acid con-

[1] Z. physik. Chem., **3**, 261 (1889).

ducts better than the salt itself. In other words, conductivity rises exceptionally rapidly with temperature and dilution. Walker[1] has also advanced a theory accounting for the increase of the "constants" with dilution. Since our data do not exhibit this phenomenon to any striking degree, a lengthy discussion of his article here would be superfluous. Briefly, he says that these amino acids are amphoteric electrolytes, and have two dissociation constants, corresponding to dissociation into acid and base.

Probably the finest example of decreasing dissociation with rise in temperature is found in the case of dichloroacetic acid—a typical strong acid. This attains maximum dissociation at $V = 1024$ at the lower temperatures, and $V = 2048$ at the higher temperatures.

The increase, with dilution, in the "constants" of bromosuccinic acid may be accounted for by the fact that the second hydrogen ion probably begins to split off at higher dilutions, and the acid behaves as if it were dibasic. White and Jones observed a similar action in case of malonic, maleic, fumaric, succinic acids, etc.

Walden[2] has carried out a careful and elaborate set of experiments with substituted malonic acids, working at only one temperature, 25°. Our results agree with his. Arranging these acids in the order of their strengths we have:

Acid	$K \times 10^4$, 25°	$K \times 10^4$, 65°
Dimethylmalonic	7.45	7.01
Butylmalonic	10.8	9.4
Ethylmalonic	12.3	10.0
Isopropylmalonic	13.2	11.3
Benzylmalonic	15.5	12.0
Allylmalonic	16.0	13.4
Malonic[3]	16.3	....
Methylethylmalonic	16.5	14.6
Diethylmalonic	74.0	50.0
Dipropylmalonic	113.0	79.0

Walden's arrangement is precisely the same, except that he

[1] Z. physik. Chem., **49**, 82 (1904).
[2] *Ibid.*, **8**, 433 (1891).
[3] Value found by Walden.

places malonic acid below methylethylmalonic. Our observations then agree with his—malonic acid is stronger than any of its monosubstituted products, and is weaker than any of the disubstituted acids, with the exception of dimethylmalonic acid. Temperature seems to have no influence on the relative strengths of the acids. There seems to be no rule governing the order in which the monosubstituted malonic acids fall. The strength of the disubstituted acids increases with increasing molecular weight, as Walden has pointed out. Combining his values and ours for disubstituted malonic acids:

Acid	Molecular weight	$K \times 10^4$, 25°
Dimethylmalonic	132	7.45
Ethylmethylmalonic	146	16.5
Diethylmalonic	160	74.0
Diallylmalonic*	184	76.0
Dipropylmalonic	188	113.0
Benzylethylmalonic*	222	146.0
Dibenzylmalonic*	284	410.0

The asterisked acids were studied by Walden.

In this connection Ostwald[1] has calculated the conductivity of benzalmalonic acid from the formula $C_6H_5CH{:}\ C(COOH)_2$. We should scarcely know whether to call it a mono- or disubstituted acid. Both hydrogens of malonic acid are replaced, but by a single bivalent group. The behavior of this acid is equally perplexing. Its constant is 40.8—higher than that of any monosubstituted acid, but too low for the disubstitution table, where its place should be between dipropyl- and benzylethylmalonic acids, according to its molecular weight, 192.

The percentage temperature coefficients of these substituted malonic acids never decreased with increasing dilution. This decrease was observed by White and Jones[2] to be a general occurrence. In this we agree with the latter investigators.

Isomeric acids have long been the subject of experimental and theoretical investigation. Why do they behave differently? Are there no definite rules governing their action?

[1] Z. physik. Chem., **3**, 369 (1889).
[2] This Journal, **44**, 198 (1910).

Ostwald,[1] Walker[2] and very recently Derick[3] have worked on the correlation of ionization and structure for such acids, and on the nature of different substituting groups.

The following relation seems to hold for a limited number of cases, which have presented themselves in this investigation:

In the case of isomeric acids containing two carboxyl groups, the acid with these groups in the "ortho" or the "cis" position is always the stronger. For example:

o-Phthalic, $K = 12.1$ *m*-Phthalic, $K = 2.87$

and again,

Maleic, $K = 154$ Fumaric, $K = 11.1$

The more hydrated an acid is in solution the less its conductivity, other things being equal. If, of two isomeric acids, the one readily forms an anhydride on coming out of solution, while the other retains the constituents of water, it seems fair to assume that the former, in solution, will be the less hydrated—and, therefore, show the greater molecular conductivity. When it comes to measuring the limiting conductivities (μ_∞) for these acids, the case is entirely different. The sodium salt of *o*-phthalic, or maleic, acid cannot form an anhydride. Therefore, in solution there is no reason why it should be less hydrated than its isomer. And since it actually shows the same molecular conductivity, it is probably hydrated to exactly the same extent. So, as has long been known, isomeric acids should have, and actually do have, the same μ_∞. The hydrated acid with a small molecular conductivity will give a smaller percentage dissociation when divided by μ_∞ than the unhydrated acid with the larger molecular conductivity, when divided by the same μ_∞. Therefore, its constant will be smaller, or, as we say, the acid will be weaker.

In the case of amino acids the proximity of the substituting groups might be expected to facilitate the formation of inner salts. In this connection we have compared results obtained for metanilic and sulphanilic acids, also for *o*- and *p*-amino-

[1] Z. physik. Chem., **3**, 170 (1889).
[2] J. Chem. Soc., **61**, 605 (1892); **67**, 147 (1895).
[3] J. Am. Chem. Soc., **33**, 1881 (1911); **34**, 74 (1912).

benzoic acids. In each case the acid with neighboring groups gives more evidence of inner salt formation than does its isomer. Under the discussion of the amino acids, we enumerated some of the characteristics due to this inner salt formation. The percentage temperature coefficients were exceptionally large; the temperature coefficients expressed in conductivity units increased with rise in temperature; the percentage dissociation increased with rise in temperature. By comparing the following data it will be seen that metanilic acid exhibits these characteristics in a more striking degree than does sulphanilic acid:

Percentage Temperature Coefficients

$V = 32$	35°–50°	50°–65°
Metanilic acid	2.66	2.23
Sulphanilic acid	2.28	1.89

Temperature Coefficients (Cond. Units)

$V = 1024$	35°–50°	50°–65°
Metanilic acid	3.45	3.82
Sulphanilic acid	4.36	4.37

Dissociatiom Constants

	0°	65°	Per cent. increase
Metanilic acid	0.90	5.33	600
Sulphanilic acid	3.28	13.4	400

Moreover, metanilic acid conducts less than sulphanilic acid; and inner salts have lower conductivity than the acids from which they are formed. This seems sufficient evidence that *m*-amino acids have greater salt-forming power than the *p*-amino acids.

By a similar comparison of the data of White and Jones[1] on *o*- and *p*-aminobenzoic acids, it will be seen that the para acid again forms less of the inner salt than does its isomer.

In the introduction of this article we stated that we would compare a few conductivity measurements made with the same acid by different investigators. Because of disagreements in the results obtained by our predecessors, we repeated the measurements for the following acids at higher temperatures.

[1] This Journal, **44**, 195–6 (1910).

Salicylic Acid, 35°. Molecular Conductivity

V	White and Jones[1]	Clover and Jones[2]	Springer
64	92.80	94.27	93.64
128	125.1	126.1	126.0
512	207.0	210.3	209.7
1024	255.4	253.3	255.0
2048	295.7	294.5	294.6

In this case our results appear to be about the mean between the results of White and Jones and those of Clover and Jones. The agreement in the results obtained with the following acid is more satisfactory:

o-Phthalic Acid, 35°. Molecular Conductivity

V	White and Jones	Clover and Jones	Springer
64	98.48	96.20	96.31
128	128.9	128.2	128.06
512	212.5	213.3	212.8
1024	259.7	258.6	258.5
2048	306.0	301.9	302.7

We have also had the opportunity of repeating measurements made by earlier investigators, and comparing our results:

Ethylmalonic Acid, 25°. Molecular Conductivity

V	Ostwald[3]	Walden[4]	Springer
32	64.5	65.07	64.42
128	115.0	117.6	114.55
512	188.0	192.0	188.9
1024	229.0	236.0	231.2

These are what we might call our average agreements. There are, of course, cases in which the difficulties are greater—an acid such as acetylsalicylic, which hydrolyzes and decomposes.

Acetylsalicylic Acid, 25°. Molecular Conductivity

V	Ostwald[5]	Springer
128	65.7	60.6
512	117.2	109.3
1024	151.5	139.3

Such a case as this, however, is really exceptional.

[1] THIS JOURNAL, **44**, 189 (1910).
[2] *Ibid.*, **43**, 213 (1910).
[3] Z. physik. Chem., **3**, 284 (1889).
[4] *Ibid.*, **8**, 449 (1891).
[5] *Ibid.*, **3**, 264 (1889).

SUMMARY

Most of the facts established by White and Jones[1] and by Wightman and Jones[2] have been confirmed by the present work. Some of the more obvious of these relations have not been discussed in detail, since reference to our data will suffice to show that they hold.

1. The percentage temperature coefficients of conductivity of the organic acids are generally small, and of the same order of magnitude, and decrease with rise in temperature.

2. The temperature coefficients, expressed in conductivity units, increase rapidly with dilution and decrease with rise in temperature. The stronger the organic acid, the larger these conductivity units.

3. The percentage temperature coefficients of the amino acids are exceptionally large, and the coefficients expressed in conductivity units increase with rise in temperature. The internal salt-forming power of these amphoteric electrolytes explains this behavior.

4. The conductivity of most organic acids is a parabolic function of the temperature, as has been pointed out by Euler[3]. This may be seen by comparing observed values with those calculated from the formula

$$\lambda = a + bt - ct^2$$

5. Change in temperature does not seem to influence the relative strengths of organic acids.

6. Strong organic acids do not obey the Ostwald dilution law.

7. Most dibasic organic acids dissociate like monobasic acids.

8. The migration velocities of the anions of organic acids are a function of the number of atoms present in the anions, and μ_∞ values for dibasic acids may be found by means of this principle.

9. The relation of dissociation of organic acids to temperature seems to be irregular. In general, the maximum disso-

[1] THIS JOURNAL, **44**, 198 (1910).
[2] *Ibid.*, **48**, 111 (1911).
[3] Z. physik. Chem., **21**, 257 (1896).

ciation has been reached at the temperatures worked with. The dissociation of only the amino acids increases at temperatures higher than 50°.

10. Isomeric acids do not behave similarly as regards change in their dissociation.

11. A relation has been found which possibly connects the behavior of some isomeric acids with their structure and power to form inner salts and anhydrides.

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SOLUBILITY AND DISTRIBUTION COEFFICIENTS OF THYMOL[1]

BY ATHERTON SEIDELL

According to the theory of alcohol narcosis developed by Meyer and Overton, the activity of a given narcotic is proportional to its coefficient of distribution between the blood and the fatty substance of the animal cells. Since it was impracticable to use these two solvents for the experimental determination of the coefficients of distribution, the problem was simplified by using water in place of the blood and olive oil as the representative of the fatty substance of the cells. This oil appears to have been chosen arbitrarily and no data are given to show that it most nearly represents the oil of the body-cells, or whether other oils would give sufficiently varying distribution coefficients to alter the observed parallelism between the narcotic action and the distribution coefficient. Experiments along this line were probably not considered necessary in the case of the narcosis theory on account of the more or less uncertainty of the observed values for the physiological activity. Furthermore, the better known plant and animal oils are composed in general of similar constituents and have fairly closely agreeing physical properties, therefore it may be supposed that the solubility of a given compound in a number of different oils would not vary significantly, and consequently the distribution coefficients would agree

[1] Presented at the 8th International Congress of Applied Chemistry, New York, Sept., 1912.

fairly satisfactorily. There are, however, so far as I have been able to ascertain, no published data on this point and consequently no estimate of the magnitude of the possible variations obtained with different oils can be made.

The opportunity to make some experiments along this line presented itself in connection with studies which are now being made in this laboratory upon thymol, a drug which is used very extensively in the treatment of hook-worm disease. This drug has been found to be superior to all other vermifuges which have so far been tried, but its use is attended with certain dangers and there is need for a safer and more efficient remedy for combatting the hook-worm. It was therefore thought that solubility and distribution studies upon thymol would serve to answer the point just raised in connection with the narcosis theory and also assist in an understanding of the manner in which thymol exerts its action in the organism.

In connection with the question as to the physiological action of thymol, it might at first be supposed that its power of dislodging the worms from the alimentary tract is due to its irritating properties, that is, that it acts mechanically and passes out of the body more or less unchanged. Against this view, however, is the fact that β-naphthol, which also has considerable effect upon hook-worms, has comparatively little volatility. Furthermore, experiments which will be described in another paper from this laboratory show that none or only a very small proportion of the administered thymol comes through the alimentary tract as such.

The solubility and distribution experiments described in the following pages were all made with the aid of a gas-heated water bath maintained at constant temperature (within $\pm 0°.05$) by means of a toluene regulator. The cork-stoppered glass vessels containing the solutions were attached to a rotating frame by the aid of which gentle agitation of the solutions was secured for periods of 18 hours or longer in all cases.

The determination of the dissolved thymol was made by the recently developed bromine-hydrobromic acid method.[1]

[1] Seidell: THIS JOURNAL, **47**, 520 (1912).

In the case of the determinations of the solubility in oils the weighed saturated solution was subjected to steam distillation and the first three distillates of about 150 cc. each were separately titrated in all cases. The complete removal of the dissolved thymol was thus assured.

The sample of thymol was the same as used for the experiments upon the bromine-hydrobromic acid method and analytical results there shown are the evidence of its degree of purity.

Although the distribution experiments were made first, the results will not be given until after the solubility determinations are described. This appears the better plan since the distribution ratios are also the ratios of the solubilities in the two solvents, and on this basis distribution coefficients in addition to those directly determined may be calculated from the solubility results.

The Solubility of Thymol in Water at Different Temperatures.— In all of the determinations an excess of thymol was rotated with about 110 cc. of water for 18 hours or longer, and 100 cc. of the clear aqueous solution were withdrawn and titrated by the bromine-hydrobromic acid method. The result at 37° is the average of five determinations. The specific gravity of the saturated solution at this temperature was found to be $d_{37}^{37} = 1.000$.

Experimental determinations		Interpolated values read from curve	
$t°$	Grams thymol per 100 grams sat. solution	$t°$	Grams thymol per 100 grams sat. solution
13	0.0737	10	0.067
15	0.0754	15	0.077
22	0.0936	20	0.088
25	0.0981	25	0.0995
29.5	0.1104	30	0.112
37.0	0.1320	35	0.126
		37	0.132
		40	0.141

A single determination reported by Zdarek[1] gives the value 0.0948 gram thymol per 100 cc. saturated solution at 19°.4.

[1] Z. anal. Chem., **41**, 227–231 (1902).

This result is about 16 per cent. too high as compared with the above values; the difference is easily explained by the fact that the Koppeschaar bromate method was used by Zdarek for the titration of the thymol and this method, as shown by my results,[1] gives high and variable results.

The Solubility of Thymol in Aqueous Hydrochloric Acid Solutions at 25°.—A series of solutions of hydrochloric acid of concentrations varying from 0.1 to 5.0 normal were prepared and an excess of thymol was added to about 150 cc. portions of each of these and the mixtures rotated at 25° for approximately 40 hours. Since preliminary experiments had shown that thymol could not be accurately determined in acid solutions brought to neutrality to phenolphthalein by the addition of caustic alkali, it was found necessary to resort to a method of steam distillation of the neutralized saturated solutions. The 100 cc. portion of the solution was therefore placed in a distilling flask of about 600 cc. capacity, 2 drops of phenolphthalein added, and fairly concentrated alkali slowly dropped in until a distinct pink color was imparted to the solution. The flask was then connected with a condenser and the distillation with a current of steam continued until three distillates of about 150 cc. each were obtained. These were each titrated by the bromine-hydrobromic acid method and the amount of dissolved thymol calculated from the used thiosulphate. The detailed results are given in the accompanying table (No. I).

The results, when plotted on cross-section paper, yield a perfectly regular curve. One determination was made at 37°.2, and this result serves as a check upon the 25° values, since the corresponding exterpolated value for the 5.0 N hydrochloric acid at 25° differs from the 37°.2 result by the same amount that was found for the difference of the solubility in water at 25° and 37°.2. Therefore a curve drawn parallel to the 25° results beginning at the figure for the solubility in water at 37°.2 and ending at the solubility in 5.0 N hydrochloric acid at the same temperature gives a close approximation to the solubility of thymol in aqueous hydrochloric

[1] *Loc. cit.*

Table I.–Solubility of Thymol in Aqueous Hydrochloric Acid Solutions at 25°

Det. No.	Solvent	d_4^{25} of the sat. solution	Vol. of sat. sol. used for distillation cc.	Distillate No.	cc. thiosulphate for Br	cc. thiosulphate for HBr	Diff.	Calc. grams thymol per 100 cc. sat. solution
1	0.1 N HCl	1.002	100	1	20.7	47.2	26.5	0.09677
				2	13.9	14.8	0.9	
				3	12.25	12.6	0.35	
2	0.5 N HCl	1.009	100	1	18.7	41.85	23.15	0.08839
				2	14.85	16.75	1.9	
				3	7.7	8.0	0.3	
3	1.0 N HCl	1.018	100	1	28.35	48.4	20.05	0.08019
				2	13.6	16.1	2.5	
				3	11.4	11.85	0.45	
4	2.5 N HCl	1.043	100	1	21.15	27.85	16.7	0.06117
				2	10.5	11.05	0.55	
				3	10.0	10.3	0.3	
5	5.0 N HCl	Dissolved thymol estimated by exterpolation = 0.0445						
5(*a*)[1]	5.0 N HCl	1.081	45.16	1	37.0	45.6	8.6	0.0772
				2	16.5	17.8	1.3	

[1] This solution saturated at 37°.2. Factor for standard thiosulphate; readings × 0.9295 = 0.05 N exactly. In the case of determination No. 5(*a*) the factor was: readings × 0.9384 = 0.05 N exactly.

acid solution at 37°.2. The values read from such a curve as compared with those actually determined at 25° are as follows:

Concentration of HCl	Gram thymol per 100 cc. sat. solution at 25°	Gram thymol per 100 cc. sat. solution at 37°.2
0.0	0.0995	0.132
0.1 N	0.0968	0.129
0.5 N	0.0884	0.121
1.0 N	0.0802	0.112
2.5 N	0.0612	0.0935
5.0 N	0.0445	0.0772

These results show that with increasing concentration of hydrochloric acid there is a regular decrease in the amount of dissolved thymol. Since the free acidity of the gastric juice of man is equivalent to approximately 0.2 per cent. hydrochloric acid, or 0.055 normal, and that of the dog is 2.7 per cent., or approximately 0.74 normal, it will be seen from the above values at 37°.2 that the diminution of the solubility of thymol in the gastric juice of man amounts to 100—0.1305/0.132 = 1.2 per cent. and the decrease in the gastric juice of the dog amounts to 100—0.1165/0.132 = 11.7 per cent.

Solubility of Thymol in Olive Oil at Temperatures between 10° and 40°.—The olive oil which was used for all of the solubility and distribution experiments was a portion of an imported sample which had been analyzed at the Bureau of Chemistry and found to be genuine and free from other oils which might be present as adulterants. The saturated solutions were prepared by rotating the oil with a sufficient excess of thymol for the periods of time shown in the accompanying table (No. II). The specific gravities were determined by means of a 10 cc. pycnometer. It was found that irregular values for the dissolved thymol were obtained if the weighed sample to be used for the steam distillation was introduced in the distilling flask in the narrow weighing bottle in which it had been weighed or even in a porcelain combustion boat. The trouble appeared to be that the oil formed globules on the inner walls of the bottle or weighing boat and these globules

were not dislodged by the current of steam. The difficulty was entirely overcome by weighing the sample from a short glass tube provided with a stopcock on the lower end. By means of this miniature burette the desired amount of the saturated solution was dropped directly into the distilling flask and its weight determined by difference. About 150 cc. of water were added and the steam distillation continued until three distillates of about 150 cc. each were obtained. These were separately titrated by the bromine-hydrobromic acid method and the dissolved thymol calculated from the sum of the thiosulphate consumed in the three titrations.

The results are shown in Table II, calculated to both the weight and volume basis of expressing the concentrations of dissolved thymol.

Table II.—Solubility of Thymol in Olive Oil at Various Temperatures

Experimental Determinations

No.	Rotation period Hrs.	$t°$	Sp. gr.[1] of saturated solution	Grams thymol per 100 grams sat. solution
1	18	13.0	0.9373	32.7
2	20	15.3	0.9370	33.5
3	18	22.0	0.9369	36.7
4	36	25.0	0.9374	40.0
5	52	29.5	0.9387	45.3
6[2]	20–60	37.3	0.9438	55.9

Interpolated Values

	Specific gravity of the		Grams thymol per 100 grams		Grams thymol per 100 cc.	
$t°$	Solvent	Sat. solution	Olive oil	Sat. solution	Olive oil	Sat. solution
10	0.9188	0.9376	46.2	31.6	42.4	29.6
15	0.9168	0.9370	50.1	33.4	46.0	31.3
20	0.9150	0.9368	56.2	36.0	51.5	33.7
25	0.9132	0.9373	66.9	40.1	61.1	37.6
30	0.9116	0.9389	84.5	45.8	77.0	43.0
35	0.9100	0.9418	111.0	52.6	101.1	49.6
37	0.9093	0.9435	124.3	55.4	112.9	52.3
40	0.9083	0.9463	151.9	60.3	137.9	57.1

[1] The specific gravities are calculated in all cases on the basis of the weight of a unit volume of water at the temperature of the experiment.

[2] Average of three determinations.

The Solubility of Thymol in Other Oils.—The method used for determining the solubilities in the several other oils was exactly the same as described above for olive oil. The results are combined in Tables III and IV and all of the curves shown in the accompanying diagram:

Table III.—Solubility of Thymol in Several Oils

Experimental Determinations

	In peanut oil		In cod liver oil		In liquid petroleum	
t°	Sp. gr. of sat. solution	Grams thymol per 100 grams sat. solution	Sp. gr. of sat. solution	Grams thymol per 100 grams sat. solution	Sp. gr. of sat. solution	Grams thymol per 100 grams sat. solution
15.3	....	....	0.945	34.6	0.8798	3.90
22.0	0.9409	42.7	0.943	35.9	0.8807	5.99
29.5	0.9392	44.9	0.9434	42.9	0.8822	13.41
37.2	0.9425	56.8	0.946	53.9	0.8886	23.32

Interpolated Values

	In peanut oil		In cod liver oil		In liquid petroleum	
t°	Sp. gr. of sat. solution	Grams thymol per 100 grams of peanut oil	Sp. gr. of sat. solution	Grams thymol per 100 grams cod liver oil	Sp. gr. of sat. solution	Grams thymol per 100 grams liquid petrolatum
10	0.9470	73.0	0.9480	50.0	0.8795	3.1
15	0.9440	73.8	0.9450	52.0	0.8798	3.95
20	0.9417	74.6	0.9435	55.5	0.8802	5.6
25	0.9399	76.4	0.9430	63.1	0.8808	9.78
30	0.9392	83.2	0.9435	77.0	0.8824	16.3
35	0.9410	106.7	0.9450	102.0	0.8860	25.5
37	0.9425	130.5	0.9460	116.5	0.8884	29.9
40	0.9450	212.5	0.9478	150.0	0.8944	38.9

Table IV.—Solubility of Thymol in Several Oils

Experimental Determinations

	In castor oil		In cottonseed oil		In linseed oil	
t°	Sp. gr. of sat. solution	Grams thymol per 100 grams sat. solution	Sp. gr. of sat. solution	Grams thymol per 100 grams sat. solution	Sp. gr. of sat. solution	Grams thymol per 100 grams sat. solution
15.3	....	...	0.943	39.12	...	....
22.0	0.9525	51.71	0.945	44.21	0.948	39.9
29.5	0.9660	57.31	0.946	52.31	0.948	43.3
37.2	0.9785	64.55	...	...	0.948	53.7

Interpolated Values

	In castor oil		In cottonseed oil		In linseed oil	
$t°$	Sp. gr. of sat. solution	Grams thymol per 100 grams castor oil	Sp. gr. of sat. solution	Grams thymol per 100 grams cotton-seed oil	Sp. gr. of sat. solution	Grams thymol per 100 grams lin-seed oil
10	0.935	81.2	0.942	56.2	0.948	62.3
15	0.942	90.2	0.943	64.0	0.948	63.1
20	0.950	101.5	0.944	74.2	0.948	65.1
25	0.958	116.5	0.945	89.4	0.948	69.0
30	0.967	137.0	0.946	113.7	0.948	78.3
35	0.975	165.0	0.948	146.5	0.948	100.0
37	0.979	180.0	0.9485	166.5	0.948	116.5
40	0.984	213.0	0.949	217.5	0.948	152.0

The Distribution of Thymol between Water and Olive Oil.—According to the general plan of the experiments, weighed amounts of thymol were added to mixtures of accurately measured amounts of oil and water, usually 10 cc. of oil and 100 cc. of water. The tubes containing these mixtures were rotated at constant temperature for approximately two days in all cases. The amounts of thymol were chosen to give very wide differences in the concentrations of the solutions. After the period of rotation the vessels containing the mixtures were removed from the bath in a large beaker filled with the water of the bath. This was done in order that the aqueous layer could be withdrawn more easily. Since it was necessary to withdraw the lower aqueous layer without simultaneously removing any of the oil, a glass tube with its lower end closed with paraffin was first introduced and the siphon tube then inserted through this. After pushing away the lump of paraffin, the end of the siphon tube was well below the oil layer and little difficulty was experienced in withdrawing nearly all of the clear aqueous solution. After ascertaining the volume, its contained thymol was determined by the bromine-hydrobromic acid method of titration. From the data thus obtained the concentration of the oil layer was calculated by difference. The specific gravity of the oil layer was ascertained by means of a specific gravity table, showing the density of various mixtures of oil and thymol at several different temperatures. These values, as determined for olive, peanut and cod liver oils, are shown in Table V. They make pos-

Table V.—Specific Gravities of Solutions of Thymol in Olive Oil, Peanut Oil and Cod Liver Oil at Various Temperatures

(The specific gravities are calculated in all cases on the basis of the weight of unit volume of water at the temperature of the experiment)

Wt. per cent. thymol in mixture	Specific gravity of solution of thymol in Olive oil at:				Peanut oil at:				Cod liver oil at:			
	13°	20°.6	29°.6	37°	13°	20°.6	29°.6	37°	13°	20°.6	29°.6	37°
0	0.9174	0.9147	0.9118	0.9093	0.9194	0.9166	0.9133	0.9109	0.9285	0.9252	0.9219	0.9198
5	0.9205	0.9177	0.9146	0.9122	0.9225	0.9195	0.9161	0.9137	0.9311	0.9277	0.9244	0.9221
10	0.9236	0.9207	0.9176	0.9151	0.9254	0.9224	0.9189	0.9165	0.9337	0.9303	0.9269	0.9246
15	0.9266	0.9238	0.9206	0.9181	0.9284	0.9252	0.9217	0.9193	0.9363	0.9329	0.9294	0.9270
20	0.9298	0.9269	0.9236	0.9211	0.9314	0.9281	0.9246	0.9222	0.9390	0.9355	0.9319	0.9295
25	0.9328	0.9300	0.9266	0.9240	0.9344	0.9310	0.9274	0.9250	0.9416	0.9381	0.9344	0.9320
30	0.9359	0.9330	0.9295	0.9270	0.9374	0.9340	0.9303	0.9278	0.9443	0.9407	0.9370	0.9344
35	0.9390	0.9361	0.9325	0.9300	0.9404	0.9368	0.9330	0.9306	0.9470	0.9433	0.9394	0.9368
40	0.9420	0.9393	0.9355	0.9330	0.9433	0.9397	0.9358	0.9334	0.9496	0.9459	0.9420	0.9393
45	0.9451	0.9423	0.9385	0.9360	0.9463	0.9426	0.9386	0.9362	0.9523	0.9484	0.9445	0.9416
50	0.9482	0.9453	0.9416	0.9390	0.9492	0.9455	0.9414	0.9390	0.9549	0.9510	0.9470	0.9441

The figures below the horizontal lines refer to supersaturated solutions.

sible the necessary calculation of the distribution results to the basis of volume concentration.

In addition to the results at 37°.2, Table VI, a series of determinations was also made at 25°. The amounts of olive oil used in the several mixtures were introduced from a weight burette instead of being measured from an ordinary burette as in all the other experiments. The calculation of the volumes of the olive oil layer was made by means of the specific gravity determinations shown in Table V. The following results were obtained (Table VII):

Table VI.—Distribution of Thymol between Water and Olive Oil at 37°.2

Composition of mixtures			Grams thymol found per 100 cc. aq. layer (C_w)	Grams thymol per 100 grams olive oil (calc. by diff.)	Grams thymol per 100 cc. olive oil layer (calc.) (C_o)	Dist. coefficient C_o/C_w
Cc. H_2O	Cc. olive oil	Grams thymol				
80	10	9.0	0.1087	97.38	46.35	427
100	10	8.0	0.1053	86.92	43.60	414
80	10	7.0	0.0987	76.12	40.67	412
80	10	6.0	0.0921	64.74	36.67	398
80	10	5.0	0.0807	55.54	33.48	415
100	10	4.0	0.0695	43.26	28.00	403
100	10	4.0	0.0682	42.96	27.93	410
100	10	2.0	0.0395	21.58	16.31	403
100	10	2.0	0.0381	21.44	16.24	426
100	10	1.0	0.0215	10.69	8.83	410
100	10	0.5	0.0122	5.37	4.64	382
100	10	0.5	0.0122	5.33	4.61	378
					Average	406

Ratio of the solubilities 52.3/0.132 = 397

Table VII.—Distribution of Thymol between Water and Olive Oil at 25°

Composition of mixtures			Gram thymol found per 100 cc. aq. layer (C_w)	Calc. grams thymol per 100 cc. oil layer C_o	C_o/C_w
Cc. H_2O.	Cc. olive oil	Grams thymol			
80	10	8.0	0.1014	44.95	443
100	10	6.0	0.0848	36.34	428
100	10	4.0	0.0655	29.43	450
100	10	2.0	0.0349	16.26	465
100	10	1.0	0.0185	8.80	474
100	10	0.5	0.0106	4.54	430
				Average	450
Ratio of the solubilities			(0.0995	37.6)	377

It will be noted that in the case of the first determination the amount of thymol in each layer is greater than the solubility at 25°, indicating, therefore, supersaturation. The distribution ratio is considerably higher than the ratio of the solubilities in oil and water. The difference is greater than can be explained on the basis of experimental error, and is probably due to an imperfect separation of the two layers. It was noted that the olive oil layers were not clear in all cases and, furthermore, that on titrating water which has been rotated with the oil, a consumption of bromine corresponding to about 1.0 cc. of 0.05 N thiosulphate per 100 cc. of the water occurred. A correction for this error would make the above observed difference in the coefficients even greater than shown.

The Distribution of Thymol between Water and Cod Liver Oil.—The determinations were made exactly as described for olive oil. In the case of the results at 37° the tubes were rotated for 2 days and allowed to stand 8 days before beginning the analysis of the aqueous layers. At 25° the time of rotation was 18 hours in the case of some and 36 hours in the case of the other tubes of the series.

Composition of mixtures			Gram thymol found per 100 cc. aq. layer (C_w)	Calc. grams thymol per 100 cc. cod liver oil layer (C_o)	C_o/C_w
Cc. H_2O	Cc. cod liver oil	Grams thymol			
Results at 37°:					
80	10	8.0	0.1099	43.81	399
80	10	5.0	0.0862	32.90	380
100	10	3.0	0.0574	22.51	392
100	10	1.0	0.0250	8.86	357
				Average	382
Ratio of solubilities			(0.132	53.3)	404
Results at 25°:					
100	10	9.0	0.1079	49.00	454
134	10	5.0	0.0816	32.58	400
160	10	2.0	0.0371	16.18	436
160	10	0.5	0.0127	4.57	359[1]
				Average	423
Ratio of solubilities			(0.0995	40.7)	409

Distribution of Thymol between Water and Peanut Oil.—A

[1] Omitted from average.

series of determinations made at 25° with peanut oil gave the following results:

Composition of the mixture			Gram thymol found per 100 cc. aq. layer (C_w)	Calc. grams thymol per 100 cc. peanut oil layer (C_o)	C_o/C_w
Cc. H_2O	Cc. peanut oil	Grams thymol			
100	10	9.0	0.1077	46.48	431
130	10	5.0	0.0786	32.45	413
160	10	2.0	0.0395	16.16	409
160	10	0.5	0.0088(?)	4.63	523[1]
				Average	417
Ratio of solubilities			(0.0995	36.5)	367

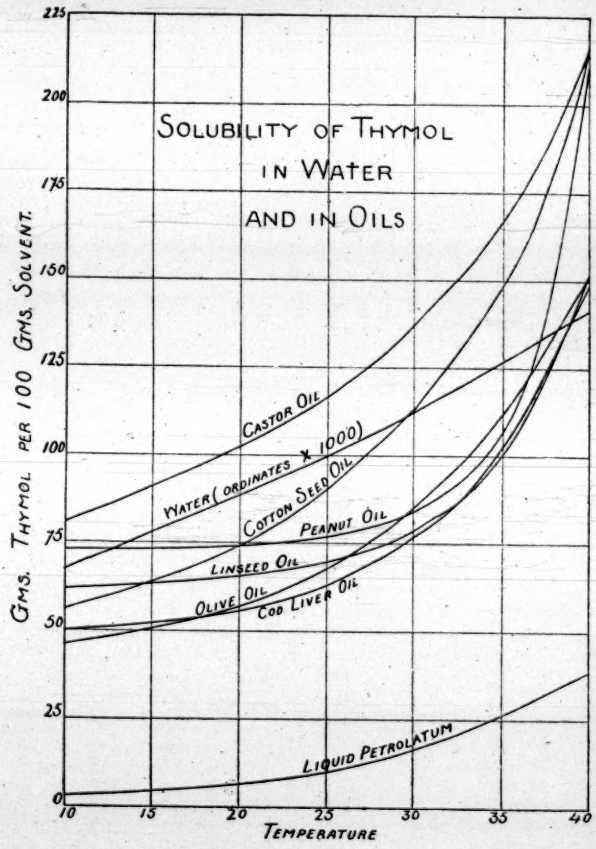
These determinations confirm those for olive oil and for cod liver oil made at 25° in that a higher distribution value is found than corresponds to the ratio of the solubilities of thymol in peanut oil and in water at this temperature. No satisfactory explanation of this difference is apparent, especially since at the higher temperature, 37°, the distribution coefficient was not found to be appreciably higher than the ratio of the solubilities. Although this difference at 25° has been found, it is apparent that both values for the coefficient cannot be correct. On account of the many analytical difficulties due particularly to the very great difference in the amounts of the thymol in the two layers and to the imperfect separation of the oil and water in some cases it would appear more rational to select, as the true distribution coefficients, the ratios of the solubilities in the two solvents. The values at 37° so obtained from the solubility results reported in the preceding tables, I to IV, inclusive, are as follows (Table VIII):

Table VIII.—Showing the Distribution Coefficients of Thymol between Water and Oils as Calculated from the Respective Solubilities at 37°.

Oil	Grams thymol per 100 cc. sat. solution in: Oil (C_o)	Water (C_w)	Dist. coefficient C_o/C_w	
Liquid petrolatum	20.4	0.132	155	
Cod liver oil	50.9	0.132	386	
Linseed oil	51.0	0.132	386	Average
Olive oil	52.3	0.132	397	393
Peanut oil	53.3	0.132	404	
Cottonseed oil	59.3	0.132	449	
Castor oil	62.9	0.132	477	

[1] Omitted from average.

Excluding the liquid petrolatum, these results show that the distribution coefficient is practically the same for four of the oils and not very different for the other two.



An examination of the diagram representing the solubilities of thymol at different temperatures shows that at lower temperatures the differences in the calculated distribution coefficient would be much greater than at 37°. However, in studies of the distribution of drugs it is their conduct at body temperature, viz., 37°, which is of particular interest and it may therefore be concluded that for this purpose olive oil is fairly representative and its selection for distribution studies is justifiable.

HYGIENIC LABORATORY
WASHINGTON, D. C.
June, 1912

REVIEWS

EXPERIMENTS IN ORGANIC CHEMISTRY. A Laboratory Manual Designed to Accompany Outlines of Organic Chemistry. By F. J. MOORE, PH.D., Associate Professor of Organic Chemistry in the Massachusetts Institute of Technology. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1911. pp. vi + 29. Price, $0.50.

This laboratory manual was prepared to be used with Prof. Moore's Outlines of Organic Chemistry in a brief course for engineering students. The experiments are therefore simple preparations that can be made in 15 laboratory periods of 3 hours each. The exercises embrace tests for nitrogen, halogens and sulphur, and the study of about 30 typical substances such as ethyl alcohol, ethyl bromide, formic acid, acetic acid, acetyl chloride, acetic anhydride, ethyl acetate, acetaldehyde and such substances.

The directions are clear and the questions make the students think. The experiment in which milk is separated into water, fat, casein and milk sugar is worthy of note. The book is a splendid one for the purpose. S. F. ACREE

TABLES ANNUELLES INTERNATIONALES DE CONSTANTES ET DONNÉES NUMÉRIQUES DE CHIMIE, DE PHYSIQUE, ET DE TECHNOLOGIE. Volume I. Année 1910. Publiées sous le patronage de l'Association international des Académies par le Comité international nommé par le VII Congrès de Chimie appliquée (Londres, juin, 1909). Paris: Gauthier-Villars; Chicago: University of Chicago Press. 1912. pp. XXX + 727. Price, bound, $6 ($6.54, postage prepaid); unbound, $5.30 ($5.82, postage prepaid).

The enormous increase in our chemical literature makes it impossible for an active investigator, or indeed anyone, to keep pace with even the few subjects in which he is interested. We must rely more and more upon the compilations of references from the literature, such as Beilstein's Handbuch der

organischen Chemie, Abegg's Handbuch der anorganischen Chemie, and the Physikalisch-chemische Tabellen by Landolt-Boernstein-Meyerhoeffer. It is certainly better for long established societies to finance and produce such volumes, and the first Tables Annuelles mark the beginning of a movement which must end in the publication and distribution of all references to chemical and physical literature and biography by an International Society.

The Table of Contents of this volume includes about 45 subjects, such as density, viscosity, radiation, electricity, atomic weights, reaction velocities, solubilities, optical rotation, conductivities, electromotive forces and mechanical constants. The names of the International Committee and of the collaborators give assurance that the data and constants published are thoroughly trustworthy, and that the best method of arrangement of the material will soon be found. The committee promises to publish the volume for 1911 before the end of 1912.

The reviewer fears that the paper and binding are too poor to withstand the wear and tear which such an important volume will receive.

S. F. ACREE

THE ANALYST'S LABORATORY COMPANION. A Collection of Tables and Data for the Use of Public and General Analysts, Agricultural, Brewers' and Works' Chemists, and Students, together with Numerous Examples of Chemical Calculations and Concise Descriptions of Several Analytical Processes. By ALFRED E. JOHNSON, B.Sc., Lond., F.I.C., A.R.C.Sc.I. Fourth Edition, Thoroughly Revised, with Additions. Philadelphia: P. Blakiston's Son & Co. 1912. pp. ix + 164. Price, $2.00.

This book, as its descriptive title suggests, contains a great deal of information and at least some of its data will be valuable to any busy chemist. The book has been carefully prepared and is printed in a handy form. It is written, however, from a British standpoint and considerable space is devoted to legal requirements and to analytical methods which do not apply to conditions in the United States and the fact is not noted that our system of weights and measures does not correspond exactly to the system used in Great Britain. For example, the U. S. gallon is not quite equal to 4 metric liters, whereas the only gallon mentioned is given as equal to 4.54596 liters. The author does not fully appreciate the proper use of significant figures. Thus, values hardly accurate to one-tenth of one per cent. are, in some cases, given to as many as eight significant figures and seven-place logarithms are used when four places would be perfectly adequate.

WILLIAM T. HALL

AN INTRODUCTION TO QUANTITATIVE ANALYSIS. By S. J. M. AULD, D.Sc. (Lond.), PH.D., F.I.C., F.C.S., Head of the Chemical Department, South-Eastern Agricultural College (University of London), Wye, Kent. London: Methuen & Co., Ltd. 1912. pp. x + 215. Price, 5 s.

The author aims to provide an introductory course suitable for college and university students which shall avoid the details of special technical analysis; and he presents the course essentially without reference to underlying theoretical considerations, except in the case of indicators for acidimetry. A general introduction (Part I) is followed by the usual course of volumetric analysis, including a chapter on gas analysis (Part II), and that by gravimetric analysis (Part III). Some typical separations and procedures for the analysis of a few representative minerals constitute Part IV, and Part V deals with vapor density determinations and some experimental work on the determination of equivalent and combining weights. The appendix includes a series of useful tables.

The subject matter is, in general, that common to many books of the same scope and purpose, and the procedures chosen are those recognized as reliable. Most of the directions are carefully and thoughtfully prepared, but the author is surely inconsistent in employing such small quantities of material for analysis as to require less than 25 cc. of the standard volumetric solutions for titrations, and in rounding out many atomic weights to whole units, while at the same time he gives his factors to five places of decimals and uses five-place logarithms. Taken as a whole, however, the book is to be commended, although it seems to lack distinctive features of its own.

The publishers would have done well to omit the insertion of their book catalogue. H. P. TALBOT

METHODS FOR SUGAR ANALYSIS AND ALLIED DETERMINATIONS. By ARTHUR GIVEN, B.S., Chemist for the Cuban Sugar Refining Co. With 8 illustrations. Philadelphia: P. Blakiston's Son & Co. 1912. pp. xi + 75. Price, $2.00.

The work is a very valuable compendium, covering a wide range of subjects in this field. The subject matter is succinctly treated, yet sufficient details are given to make certain the proper method of procedure. The book has been written and arranged for the analyst rather than the investigator, and is particularly adapted to the needs of young chemists who are well grounded in the fundamentals, yet new to the subject. As Assistant Chemist in the Bureau of Chemistry, U. S. Department of Agriculture, the author had an excellent opportunity to make a comparative study of the numerous

methods followed by different workers in this field. As a result, he has presented in most cases but a single method of analysis for each substance, and that method as a rule represents the best practice. Fairly complete references are given to more extended treatises, and about thirty pages have been devoted to standard tables. The entire work has been divided into 118 numbered parts, the numbers serving to identify the divisions throughout the work, thereby making for condensation and easy references. In common with most writers on this subject, the author has neglected to state the limitations of the methods given. The binding, printing, paper, etc., are excellent.

FREDERICK BATES

KOLLOIDCHEMIE. Ein Lehrbuch von RICHARD ZSIGMONDY, Professor an der Universität Göttingen, Direktor des Instituts für anorganische Chemie. Mit 37 Figuren im Text. (Chemische Technologie in Einzeldarstellungen, herausgegeben von PROF. DR. FERDINAND FISCHER.) Leipzig: Verlag von Otto Spamer. 1912. s. xi + 294. Preis: geh., M. 15; geb., M. 17.

This contains a brief (pp. 1–85) introduction and elementary discussion of the properties and chief characteristics of colloids, their classification, and the theory of peptization, followed by a special part giving in considerable detail the preparation and properties of colloidal metals, nonmetals, oxides, sulphides, inorganic and organic salts, dyes, albumin, gelatin, hemoglobin and casein. The author explains in the preface that the difficulty of correctly generalizing so new and broad a field as colloid chemistry has led him to make the general discussion rather brief and of limited scope, and to bring out in the descriptions of the individual colloids the properties which have been discovered through the study of that particular material. The book follows this scheme conscientiously, giving quite complete descriptions of the work on individual colloidal materials, and in this respect is most satisfactory, but in the general discussion one feels that much has been sacrificed for the cause of brevity. The book is a valuable addition to the literature of colloid chemistry, is in no wise a duplicate of such books as Ostwald's or Freundlich's, and will serve perhaps as a basis for the more theoretical treatment of those authors.

H. ISHAM

CHEMICAL WORKS. Their Design, Erection and Equipment. By S. S. DYSON and S. S. CLARKSON. London: Scott, Greenwood & Son; New York: D. Van Nostrand & Co. 1912. pp. xii + 207. Price, $7.50.

This book, divided into 11 chapters dealing with the design and equipment of chemical works, is of considerable interest.

The following subjects are considered: Choice of site, materials of construction and the general layout of works, the power plant, sulphuric, nitric and hydrochloric acid plants, sulphate of ammonia, artificial manure and high explosive plants, apparatus used in chemical plants, and appendix matter touching on the chemical engineer, the English Alkali Works Regulation Act, and welfare work or "Prosperity Sharing."

The most valuable part of the book is to be found in the description of plants for the manufacture of acids and other heavy chemicals enumerated. Scale drawings are given, and these are accompanied by descriptive matter, hints, etc., which give some valuable information. It would seem better to have had a set of specifications to accompany the drawings instead of giving the details in a more or less rambling description.

The contact process for the manufacture of sulphuric acid is only referred to in a few words as being inapplicable to England.

The recent improvements in the manufacture of this acid by the Chamber process are mentioned, but not embodied in the plan of the works as given by the authors.

The matter presented in the choice of site is a statement of common sense facts as to location, transportation facilities, etc., which might be presupposed in anyone who contemplated the erection of a chemical plant. Under "Power Plant" we find information which appears in any good book on mechanical engineering, a great part of the space being devoted to a description of the Parson steam turbine.

The authors point out the fact that electricity is being used more and more in chemical works, but the subject is not otherwise touched upon.

Considerable stress is laid on apparatus for fire prevention, but automatic sprinklers are not mentioned.

Under the head of "General Plant" is given a description of apparatus used in chemical plants such as centrifugals, filter presses, acid lifts, etc., which may be found in most up-to-date books on chemical engineering or the catalogues furnished by the manufacturers. An exception, however, appears in reference to the use of apparatus constructed of fused silica, which finds many applications in the manufacture of acids and is well described here.

The appendix matter is concerned with the English act regulating the manufacture of heavy chemicals and welfare work.

It is doubtful whether these subjects will be of much value to the chemical engineer in this country.

We believe that the new matter presented in this book is comparatively small and the price charged for the publication will prevent many from making use of it. SAMUEL A. TUCKER

DAS ERDÖL, SEINE PHYSIK, CHEMIE, GEOLOGIE, TECHNOLOGIE UND SEIN WIRTSCHAFTSBETRIEB. In fünf Bänden. Unter Mitwirkung von DRS. AISINMAN, ALBRECHT, GOULESCHAMBAROFF, HOLDE, HOLOBEK, KAET, LOSSEN, KOETTNITZ, SINGER, UBBELOHDE, WISCHIN und WOLFF, herausgegeben von C. ENGLER, o. ö. Professor an der Techn. Hochschule zu Karlsruhe, und H. VON HÖFER, o. ö. Professor an der Montanistischen Hochschule zu Leoben. I. Band, Erste Abteilung. Die Chemie und Physik des Erdöls, bearbeitet von C. ENGLER. Leipzig: Verlag von S. Hirzel. 1912. pp. xiv + 593. Price, M. 28.

This is the most recent, most exhaustive and most authoritative treatment of this subject that has appeared. Nothing apparently has been omitted, nor it is strange when one considers the authors, Profs. Engler and von Höfer. It should be readily accessible to all those who wish to know the subject of petroleum thoroughly. A. H. GILL